

For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAENSIS





Digitized by the Internet Archive
in 2019 with funding from
University of Alberta Libraries

<https://archive.org/details/gashydratesinnit00jmh>

11-2-63
1963
30

THE UNIVERSITY OF ALBERTA

"GAS HYDRATES IN THE NITROGEN-METHANE SYSTEM"

BY

J.M. JHAVERI

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

FACULTY OF ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

EDMONTON, ALBERTA

MARCH, 1963

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled "Gas Hydrates in the
Nitrogen-Methane System" submitted by J.M. Jhaveri in
partial fulfillment of the requirements for the degree
of Master of Science in Chemical Engineering.

ABSTRACT

Gas hydrate equilibrium curves for the ternary system $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ were obtained. The hydrate-forming conditions of pure nitrogen, pure methane and of six mixtures of nitrogen and methane have been investigated in the temperature interval 32°F to 72°F and between pressures of 300 and 5100 psia.

The pressure-composition equilibrium diagrams at 32°F , 39.7°F and 44°F for the ternary systems were also obtained. The information thus obtained was used to evaluate vapour-solid equilibrium constants for methane and nitrogen. With the set of equilibrium constants so obtained curves representing the equilibrium constants for methane were extended in the region where the values of equilibrium constants for methane are less than unity.

The solid-solution theory of Platteeuw and Van der Waals was applied to predict the pressure-composition diagrams for the system at 32°F . The theory was also applied to predict pressure-composition diagrams for the ternary systems $\text{CH}_4\text{-C}_2\text{H}_4\text{-H}_2\text{O}$ and $\text{CH}_4\text{-C}_2\text{H}_6\text{-H}_2\text{O}$. The phase-diagrams thus obtained also gave the solid vapour equilibrium constants for CH_4 . The experimental

values of the equilibrium constant fell below the theoretical values at pressures of about 100 psia, coincided with the theoretical values at about 400 psia, and fell about 25 per cent above the theoretical values at pressures in the region of 1500 psia.

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Dr. D.B. Robinson for his guidance through creative suggestions, and keen interest in this project.

Co-operation and services received from Mr. F. Butz and his staff in building the equipment are very much appreciated. My thanks are also extended to Mr. K. Balcombe for supplying materials needed from time to time.

Co-operation received from the staff of the computing centre of the University of Alberta is greatly appreciated.

Financial assistance made available from the National Research Council is gratefully acknowledged.

TABLE OF CONTENTS

	page
List of Tables	i
List of Figures	ii
INTRODUCTION	1
THEORY	
A Phase Equilibria in Gas Hydrates	9
B Statistical Mechanical Theory Applied to Hydrate Formation	15
C Evaluation of Langmuir Constants	22
EXPERIMENTAL PROGRAMME	
A Equipment	26
B Experimental Technique	34
C Technique for the Determination of Initial Hydrate Forming Conditions	35
D Technique for the Determination of Pressure- Composition Diagram for N ₂ -CH ₄ -H ₂ O System	36
EXPERIMENTAL RESULTS	
A Initial Hydrate Forming Conditions	39
B Pressure-Composition Diagrams	43

THEORETICAL CALCULATIONS	49
DISCUSSION OF RESULTS	
A Initial Hydrate Forming Conditions	62
B Pressure Composition Diagrams	66
OUTLINE FOR FUTURE WORK	72
NOMENCLATURE	74
BIBLIOGRAPHY	76
APPENDIX	
A Calculation of Compressibility Factors for Nitrogen-Methane Mixtures	79
B Determination of the Composition of the Hydrate Phase by Material Balance	84
C Chromatographic Analysis	89
D Tabulations	93
E The Computer Programme for the Determina- tion of the Pressure Composition Diagram	104

LIST OF TABLES

		page
I	Experimental Data on Initial Hydrate-Forming Conditions for the $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ System	93
IA	Isothermal Data on Initial Hydrate-Forming Conditions	95
IB	Isobaric Data on Initial Hydrate-Forming Conditions for the $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ System	96
II	Experimental Pressure Composition Data for the $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ System at 32°F	97
III	Experimental Pressure Composition Data of the $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ System at 44°F	98
IV	Experimental Pressure Composition Data for the $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ System at 39.7°F	99
V	Pressure Composition Data for the $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ System at 32°F From Theory	100
VI	Pressure Composition Data for the $\text{CH}_4\text{-C}_2\text{H}_6\text{-H}_2\text{O}$ System at 32°F From Theory	101
VII	Pressure Composition Data for the $\text{CH}_4\text{-C}_2\text{H}_4\text{-H}_2\text{O}$ System at 32°F From Theory	102
VIII	Compressibility Factors of Nitrogen and Methane Along the Hydrate-Equilibrium Curves	103

LIST OF FIGURES

	page
1 The Small and Large Cavities of Structure I	7
2 The Large Cavity of Structure II	8
3 Schematic Phase-Diagram of Hydrates Exhibiting no Temperature Limit	12
4 Schematic Phase-Diagram of Hydrates Exhibiting a Temperature Limit	14
5 Schematic Diagram of the Equipment	27
6 The Equilibrium Cell	29
7 Rotary Seals	32
8 The Assembly of the Equipment	33
9 Initial Hydrate Forming Conditions for $N_2-CH_4-H_2O$ System	40
10 Isothermal Data on Initial Hydrate Forming Conditions	41
11 Isobaric Data on Initial Hydrate Forming Conditions	42
12 Pressure-Composition Diagram for the $N_2-CH_4-H_2O$ System at $32^{\circ}F$ (Experimental)	44
13 Pressure-Composition Diagram for the $N_2-CH_4-H_2O$ System at $44^{\circ}F$	45
14A Pressure-Composition Diagram for the $N_2-CH_4-H_2O$ System at $39.7^{\circ}F$	46
14B Pressure-Composition Diagrams for the $N_2-CH_4-H_2O$ System	47
14 Pressure-Composition Diagram for the $N_2-CH_4-H_2O$ System at $32^{\circ}F$ (Theoretical)	53

		page
15	Pressure-Composition Diagram for the $\text{CH}_4\text{-C}_2\text{H}_6\text{-H}_2\text{O}$ System at 32°F (Theoretical)	54
16	Pressure-Composition Diagram for the $\text{CH}_4\text{-C}_2\text{H}_4\text{-H}_2\text{O}$ System at 32°F (Theoretical)	55
17	Equilibrium Constants for Methane	57
18	Equilibrium Constants for Nitrogen	58
19	Equilibrium Constants for Methane at 32°F	60
20	Compressibility Factors of Nitrogen and Methane Along the Hydrate Equilibrium Curves	65
21	Compressibility Factors of $\text{N}_2\text{-CH}_4$ System at 44°F	83
21A	Compressibility Factors of $\text{N}_2\text{-CH}_4$ System at 32°F	82
22	Effect of Nitrogen on the Equilibrium Pressure	67
23	Chromatograph Calibration Curves for Nitrogen and Methane	90
24	Iron-Constantan Thermocouple Calibration	91

As a result of this work it is established that gas-hydrates grow in two structures, referred to as Structure I and Structure II. In these structures, gas molecules are entrapped in cavities formed by water molecules linked together by hydrogen bonding. There are two types of cavities in each structure and one of them is considerably smaller than the other. Depending on the size of the molecule (maximum molecular dimension) the gas will occupy the smaller or larger cavities. Details of the cavity geometry are given below⁽²⁸⁾. Figure 1 and 2 describe the shape of the cavities.

Smaller Cavities:- (Pentagonal dodecahedra)

	Average diameter
Structure I	5.10 Å ^o
Structure II	5.00 Å ^o

Large Cavities:- (Tetrakai decahedra)

Structure I	5.80 Å ^o
Structure II	6.70 Å ^o

Dimensions of the cavities immediately restrict the number of gases which can form hydrates. Any gas having a molecular dimension larger than 6.7 Å^o cannot form hydrates. Theoretically there cannot be any restriction on the smaller molecules. However, it is found that smaller molecules like

hydrogen and helium are not retained within the frame very strongly. Gases with a hydrogen atom in a polar-bond do not form hydrates. Halogen acids, alcohols, amines, organic acids, amides and ammonia do not form hydrates for the same reason.

The first four members of the paraffinic hydrocarbons have molecular dimensions suitable to be enclosed in cavities of Structure I and Structure II. Hydrates of methane, ethane, and other saturated and unsaturated hydrocarbons have been known for a long time. Initial hydrate forming conditions of these gases have been studied by many workers^(4, 6, 7, 8). To study the effect on hydrate forming conditions of one gas in the presence of another gas, many ternary systems have been investigated. Deaton and Frost⁽⁵⁾ studied the hydrate-forming conditions in the ternary systems, methane-ethane-water and methane-propane-water. The hydrate forming conditions of binary mixtures of methane and other gases were studied by Katz and co-workers^(12, 26). A common trend clearly emerges out of the results obtained on the above systems.

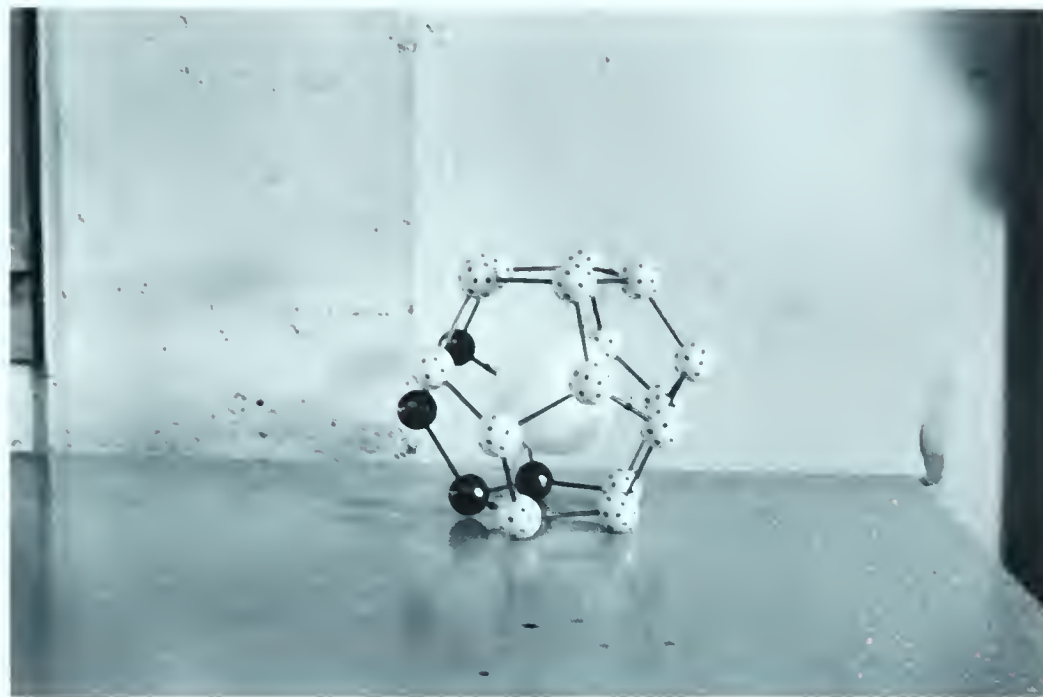
Van Cleeff and Diepen⁽²⁷⁾ investigated the hydrate forming conditions of nitrogen and oxygen and introduced these two permanent gases of atmosphere in the list of potential hydrate formers. As nitrogen is one of the constituents of

the natural gas, it was decided to study the initial hydrate forming conditions of a ternary system $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$. In the ternary systems previously studied, whenever methane was present it was the lighter component whereas in the system under investigation methane is the heavier component.

Wilcox, Carson and Katz⁽³³⁾ indicated that gas hydrates behave to some extent as solutions of gases in crystalline solids, and put forward the concept of vapour-solid equilibrium constants which can be effectively used to predict the hydrate forming conditions of multi-component mixtures. By definition, an equilibrium constant is a ratio of the mole fraction of a particular component in the gas phase to that in the hydrate phase on a water-free basis. Consequently the equilibrium constant for the lightest component in a multi-component mixture will always be greater than unity. Equilibrium constants for methane obtained from the study of various ternary systems were all greater than unity, since methane was the lightest component. One of the objectives of this investigation was to provide equilibrium constants for methane in a system where it was the heavier component. This would make it possible to extend the curves prepared by Carson and Katz⁽¹⁾, depicting the equilibrium

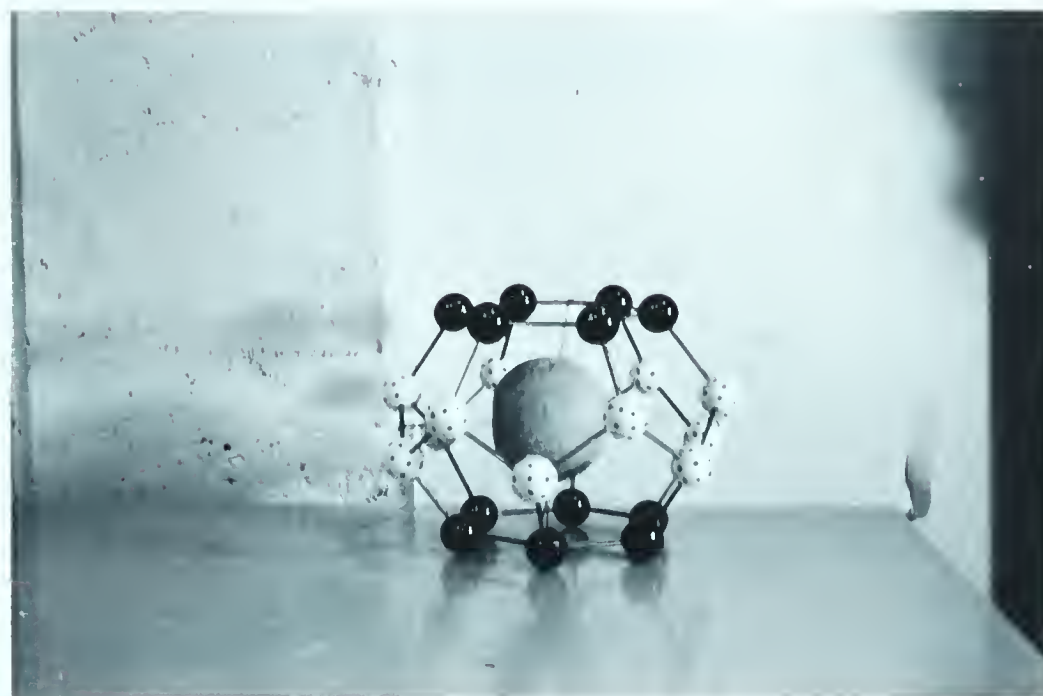
constants of methane as a function of temperature, in a region where the value of equilibrium constant is less than unity.

MAR • 63



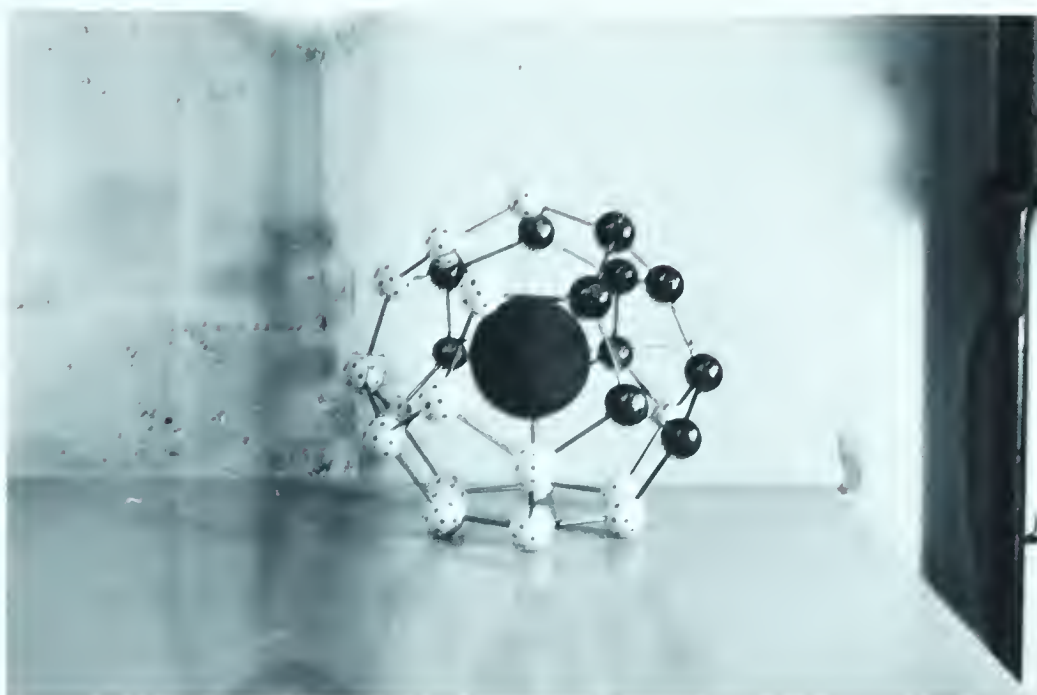
THE SMALL CAVITY OF STRUCTURE I

MAR • 63



THE LARGE CAVITY OF STRUCTURE I

MAR • 63



THE LARGE CAVITY OF STRUCTURE II

FIGURE 2

THEORY

Phase Equilibria in Gas Hydrates

The study of gas-hydrates essentially involves the study of various phases in equilibrium at different conditions of pressure and temperature. Depending on the critical temperature of the hydrate former, and the working temperature there may be three or four phases in equilibrium. Below the ice point the phases which can be in equilibrium are hydrate, ice, vapour and liquid phase rich in hydrate former. The phase which can be in equilibrium above the ice point are hydrate, water rich liquid, vapour and a liquid phase rich in hydrate former. The total number of phases present at any instant will depend on the number of degrees of freedom of the system, which can be easily predicted from Gibb's phase rule stated mathematically as follows:

$$F + P = C + 2$$

where F = number of degrees of freedom

P = number of phrases present

C = number of components

Thus in a binary system, univariant equilibria allow the presence of only three phases, whereas in a ternary system

four phases may be present.

The following generalization is thought to be of great help in a better understanding of the phase equilibria. (18)

"The addition of a component to a system adds a degree of freedom to all features represented for the system. In other words, areas will generate volumes, lines will generate surfaces, and points will generate lines. These features will have one extra degree of freedom but will not be changed in designation. That is, a point representing vapour, solid and liquid in equilibrium for a one component system will generate a line in space on the addition of a second component, but this line will represent equilibrium between the same phases. Similarly a line representing vapour, liquid equilibrium will generate a surface which will represent a liquid saturated with vapour. Associated with each surface there must be another surface representing vapour saturated with a liquid".

Termination of a phase-equilibrium is brought about by the addition of a phase, by the loss of a component or by an attainment of a critical point. The effect brought about by an addition of a phase or by the loss of a component is to decrease the number of degrees of freedom of the system by one. Thus in both the cases the prevailing phase-equilibrium is terminated. The appearance of a solid phase brought about by cooling a one component system consisting of two phases, liquid and vapour, down to its triple point terminates the two phase equilibrium, and the system becomes invariant. In

a purely physical process it is not possible for a closed system to lose a component. A thermodynamic system may however lose a component in a physico-chemical process under the influence of the external variables, with the loss of a degree of freedom which eventually leads to the termination of the particular phase equilibrium. Termination of the phase equilibrium by an attainment of a critical point is very common in phase-equilibrium studies. Due to the loss of identity of the two distinct phases - vapour and liquid - at the critical point the prevailing vapour-liquid equilibrium is terminated.

Phase Equilibria in a Binary System

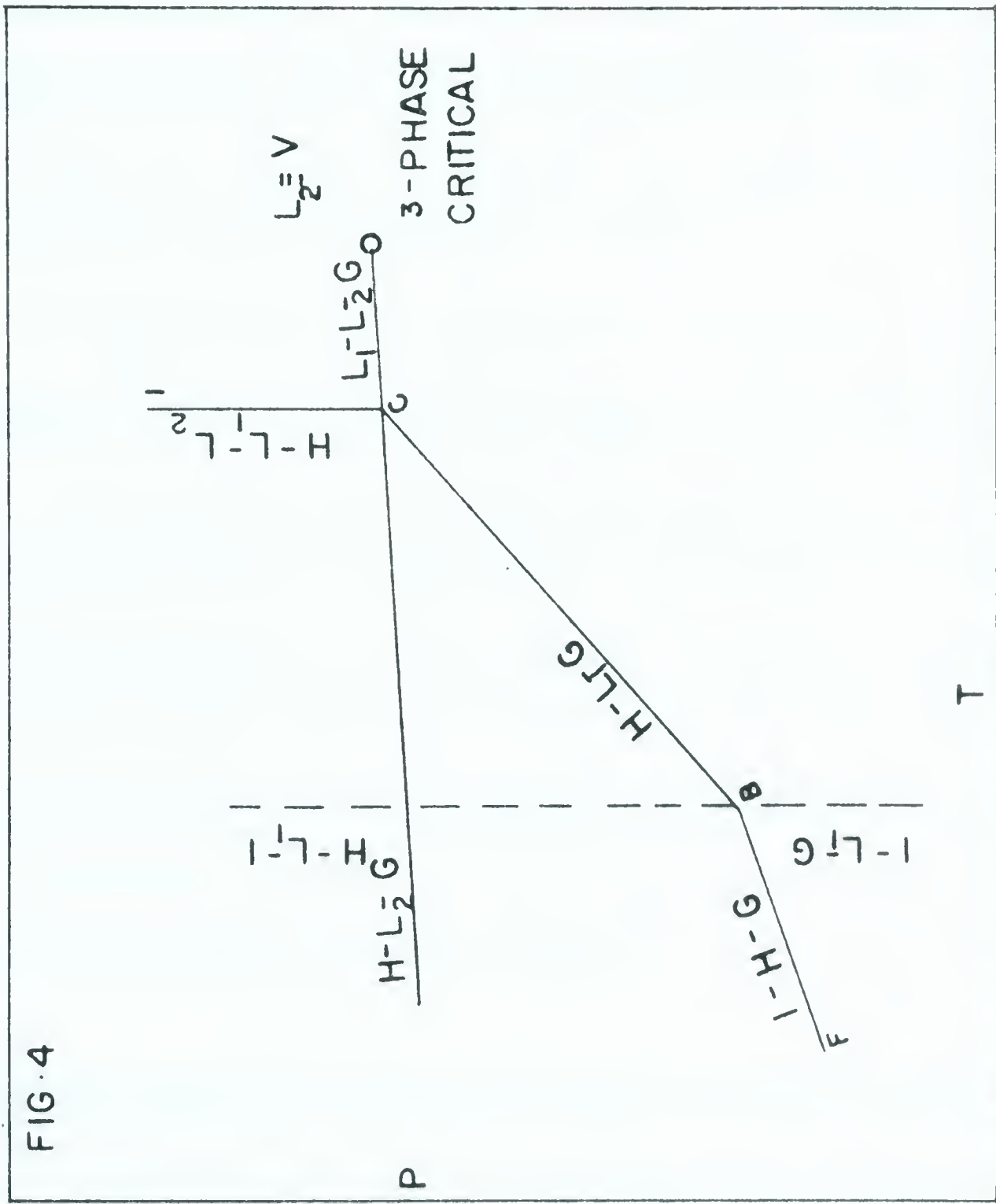
Figure 3 is a phase equilibrium diagram of a binary system consisting of a hydrate former and water. Lines BC and BF indicate the univariant equilibria with three phases in equilibrium. Along BC, three phases - hydrate, water-rich layer and gas - are in equilibrium. No hydrate will exist below BC and BF, while above BC and BF, hydrate and excess phase will be present. Figure 3 is a typical pressure-temperature diagram for a hydrate former whose critical temperature is considerably below the working temperature. Methane-water, and ethylene-water are typical of systems exhibiting the phase behaviour indicated in this figure.

Figure 4 is a binary phase diagram for a hydrate-former whose critical temperature is considerably above the freezing point of water. Lines BC and BF represent the same phases in equilibrium as in Figure 3. The point C is of particular significance as it is invariant.

Four phases in equilibrium at C are hydrate, water-rich layer, hydrocarbon rich layer and gas. The three phases in equilibrium along CI are hydrate, water rich layer, and hydrocarbon rich layer. Ethane-water, and propane-water, are typical systems exhibiting the phase behaviour indicated in Figure 4.

Phase Equilibria in Ternary Systems

The addition of a component leads to an additional degree of freedom for the system. A ternary system has one degree of freedom more than a binary system. This additional degree of freedom is the variable composition of the system. Depending on the total composition of the system the hydrate will melt over a range of temperatures at a fixed pressure. Similarly there will be a range of decomposition pressures at a fixed temperature.



SCHEMATIC PHASE-DIAGRAM OF HYDRATES EXHIBITING A
TEMPERATURE LIMIT

Quadruple points in a ternary system are univariant and not invariant as in the case of a binary. There exists an unique quadruple point for every composition. As a result there is a line of four phase equilibrium instead of a single point as in the case of a binary.

Hydrate forming conditions in a ternary system can be studied either by keeping the composition or temperature fixed. In a ternary system, the three phase equilibrium is univariant at constant composition. As a result, a family of pressure-temperature curves each at a constant composition reveals the general hydrate forming tendency of the system. Ternary systems may also be studied by determining the isothermal pressure-composition diagrams, which elucidate the general phase behaviour quite clearly.

Statistical Mechanical Theory Applied to Hydrate Formation

Van der Waals and Platteeuw⁽²⁹⁾ developed the solid solution theory for hydrates on the basis of statistical mechanical principles. Thermodynamic properties of hydrates were derived from a simple model which corresponds to the three dimensional generalization of ideal localized adsorption. The structural frame formed by water molecules by hydrogen bonding

is stabilized only by the gas molecules occupying the cavities. The empty host lattice is metastable and does not exist as such. The ordinary crystal lattice (liquid water or ice) is termed the α modification and the metastable lattice is called β . The mathematical analysis presented in this chapter is based on the following assumptions.

(1) The contribution of the water molecules to the free energy is independent of the mode of occupation of the cavities. This excludes the case of large molecules which might disturb the lattice.

(2) The mutual interaction of the solute molecules is neglected, i.e. the partition function of a solute molecule in the cage is independent of the number and types of the solute molecules present.

(3) The encaged molecules are localized in the cavities and a cavity can never hold more than one solute molecule.

(4) Classical statistics are valid.

The behaviour of the solute molecules in the cavity is represented satisfactorily by the four assumptions given above. The objection raised against the second assumption is waived on the basis of the information obtained from the numerical calculations and experimental evidence. The solute

solute interaction to the configurational energy is at the most a few percentage of the energy of binding of the solute molecules in the cages.

Partition Function

Mathematically a partition function is given by the following relation:

$$P.F. = Q = \sum_i g_i e^{-\epsilon_i/kT} \quad (1)$$

where

g_i = degeneracy of the energy state i

ϵ_i = energy in the state i

k = Boltzmann's constant

T = absolute temperature

Following are the relations connecting partition function with the thermodynamic properties.

$$F = -RT \ln \frac{Q}{N} + 1 - V \frac{\ln Q}{V} \quad (1a)$$

$$H = RT \frac{\ln Q}{\ln T} + \frac{\ln Q}{\ln V} \quad (2)$$

where

F = free energy/mole

H = enthalpy/mole

V = volume of the assembly

N = Avogadro's constant

Depending on the relations of the system with the surroundings, it may be necessary to use one of the three kinds of partition functions given below:

- (1) Micro canonical
- (2) Canonical
- (3) Grand canonical

The microcanonical partition function or sometimes known as the system partition function is the summation represented in Equation 1 for an individual particle. A system in statistical mechanics is used to describe microscopic entities like atoms, molecules, ions and photons.

The Canonical partition function (sometimes known as assembly partition function) is a multiple of the partition functions for the individual systems.

$$(P.F.)_{\text{assembly}} = Q^N \quad (3)$$

An assembly in statistical mechanics consists of a large number of systems, and it corresponds to a thermodynamic system.

The grand canonical partition function (usually abbreviated to G.P.F.) is given by the following relations.

$$G.P.F. = \sum_{(N)} (P.F.)_N \lambda^N \quad (4)$$

where ,

$(P.F.)_N$ = Assembly partition function

λ = Absolute activity of a system in
assembly.

Application of the Theory of G.P.F. to Clathrates

A clathrate consists of a cage forming substance and a solute. The partition function of a clathrate can be represented as a multiple of two partition functions as follows:

$$(P.F.)_{\text{clathrate}} = (P.F.)_Q \times (P.F.)_J$$

where

$(P.F.)_Q$ = partition function of a cage forming
substance

$(P.F.)_J$ = partition function of the enclosed
molecules

$$(P.F.)_Q = \exp (- F^{\beta} / kT)$$

$$(P.F.)_J = \prod_i \left(\frac{\gamma_i^{N_Q} !}{(\gamma_i^{N_Q} - \sum_J N_{Ji}) ! \prod_J N_{Ji} !} \prod_J h_{Ji}^{N_{Ji}} \lambda_J^{N_{Ji}} \right) \quad (5)$$

$$G.P.F. = \exp (- F^{\beta} / kT) \sum_{N_{Ji}} \prod_i \left[\frac{(\gamma_i^{N_Q}) !}{(\gamma_i^{N_Q} - \sum_J N_{Ji}) ! \prod_J N_{Ji} !} \prod_J h_{Ji}^{N_{Ji}} \lambda_J^{N_{Ji}} \right] \quad (6)$$

where

γ_i = number of cavities of type i per molecule of Q

h_J = partition function of a J molecule when encaged
in a type i cavity.

Equation 6, after summing with the help of a multinomial theorem, takes the following form

$$\text{G.P.F.} = \exp(-F^\beta/kT) \prod_i (1 + \sum_J h_{Ji} \lambda_J)^{\gamma_i N_Q} \quad (7)$$

Composition of the clathrate is given by the following relation

$$N_K = \sum_i N_{Ki} = \lambda_K \left(\frac{\partial \ln \text{G.P.F.}}{\partial \lambda_K} \right)_{T, V, N_Q, \lambda_J} \quad (8)$$

Differentiating Equation 7 with respect to λ_K and substituting the result in Equation 8, the following equation is obtained:

$$Y_{Ki} = \frac{N_{Ki}}{N_Q \gamma_i} = \frac{h_{Ki} \lambda_K}{(1 + \sum_J h_{Ji} \lambda_J)} \quad (9)$$

where

$$\lambda_K = \frac{P_K}{kT \Phi_K(T)} \quad \text{and} \quad \Phi_K(T) \text{ is the molecular}$$

partition function of gaseous K with the volume factor removed.

Now

$$Y_{Ki} = \frac{C_{Ki} \cdot P_K}{(1 + \sum_i C_{Ji} \cdot P_J)} \quad (10)$$

where

$$C_{ki} = \frac{h_{ki} \lambda_k}{P_k} \quad (10A)$$

Therefore,

$$1 - \sum_K Y_{Ki} = (1 + \sum_J C_{Ji} P_J)^{-1} \quad (11)$$

Differentiation of Equation 6 with respect to N_Q generates the following equation:

$$- \left(\frac{\partial \ln G.P.F.}{\partial N_Q} \right)_{T, V, \lambda_J} = \frac{\mu_Q^\beta}{kT} - \sum_i \gamma_i \ln(1 + \sum_J h_{Ji} \lambda_J) \quad (12)$$

where

$$\mu_Q^\beta = \frac{\partial (F^\beta)}{\partial N_Q} \text{ is the chemical potential of } \beta \text{ modification.}$$

Substituting $(1 + \sum_J C_{Ji} P_J)^{-1}$ for $(1 + \sum_J h_{Ji} \lambda_J)^{-1}$

in Equation 12, one obtains,

$$\mu_Q = \mu_Q^\beta - kT \sum_i \gamma_i \ln(1 + \sum_J C_{Ji} P_J) \quad (13)$$

Equations 11 and 13 are very important relations connecting vapour pressure, composition and chemical potential of the solvent in a clathrate, obeying the present model.

The careful inspection of Equation 10 reveals the similarity it holds with the Langmuir isotherm. The Langmuir adsorption isotherm may be represented as follows,

$$\theta = \frac{c_1 \cdot p}{1 + c_2 \cdot p}$$

where

c_1 , c_2 are constants, p is total pressure of the gas phase and θ is the fraction of the surface area covered by adsorbed gas molecules.

Equation 10, when written for a single component gas phase, takes the following form,

$$y_i = \frac{C_i p}{1 + C_i P}$$

The langmuir isotherm has been applied to a number of cases of adsorption on solid surfaces, however it has its own limitations. The constant ' C_{k_i} ' will be referred to as a Langmuir constant.

Evaluation of Langmuir Constants

As shown earlier by Equations 9 and 10, the Langmuir constant has been defined as a function of h_{ji} . Evaluation of h_{ji} requires a method to calculate the potential energy of a solute molecule in the cavity. In addition to translational and rotational energy of the molecule there is an interaction energy which should be included in the partition function.

The theory introduced by Lennard-Jones and Devonshire for the study of liquids provides a powerful method for the quantitative evaluation of the partition function of a solute molecule within its cavity.

The following two assumptions in addition to the four assumptions cited earlier, are implied in the L-J-D theory:

(5) The solute molecules can rotate freely in their cavities. (i.e. The rotational partition function in the cavity is the same as that in the gas phase).

(6) The potential energy of a solute molecule when at a distance r from the centre of its cage is given by the spherically symmetric potential $w(r)$, proposed by Lennard-Jones and Devonshire.

The assumptions given above restrict the applicability of this theory to the monatomic gases like argon, krypton, and xenon. Rotation of diatomic molecules in a cavity is actually constrained due to their non-spherical shape. Hindered rotation of molecules like oxygen and nitrogen tends to decrease the entropy and as a result the vapour pressure of such molecules is raised.

The Lennard-Jones 6-12 potential evaluates the average contribution to the potential energy due to the interaction

of a solute molecule with any of the elements constituting the wall of its cage. The energy of interaction is given by the following equation:

$$\phi(R) = 4 \epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

Lennard-Jones-Devonshire⁽¹¹⁾ summed the interactions over Z molecules distributed over the surface of a sphere and so obtained a function $w(r)$ describing the resulting field.

Within the sphere averaged over all orientations,

$$w(o) = Z \epsilon \left[\bar{\alpha}^4 - 2 \bar{\alpha}^2 \right] \quad (14)$$

$$w(r) - w(o) = Z \epsilon \left[\bar{\alpha}^4 l(y) - \bar{\alpha}^2 \cdot 2 \cdot m(y) \right] \quad (15)$$

$$l(y) = (y^4 + 12y^3 + 25.2y^2 + 12y + 1)/(1 - y)^{10} - 1$$

$$m(y) = (1 + y)/(1 - y)^4 - 1$$

where

$$y = (r/a)^2, \sigma, \epsilon \text{ are the molecular parameters,}$$

and α is a parameter which measures the cell radius 'a' in terms of molecular diameter σ . Mathematically

$$\alpha = \frac{a^3}{\sqrt{2} \sigma^3}$$

With the assumptions (5) and (6) the cell partition

function can be represented as,

$$h = \phi(T) \exp \left[- \frac{w(o)}{RT} \right] \int_{\text{cell}} \exp \left[- \frac{w(r) - w(o)}{kT} \right] 4\pi r^2 dr \quad (16)$$

$\phi(T)$ represents the contributions due to translational and internal degrees of freedom of the solute molecule. The second term represents the potential energy $w(o)$ of the solute molecule at the centre of its cage referred to the perfect gas, and the integral is the free volume of the solute molecule wandering in the cavity. In order to conform with the customary notation of the L-J-D theory the free volume may be written as $2\pi a^3 g$, where the function 'g' stands for the dimensionless integral,

$$g = \int \exp \frac{Z \epsilon}{kT} \left[- \frac{1(y)}{\alpha^4} + \frac{2m(y)}{\alpha^2} \right] y^{\frac{1}{2}} dy \quad (17)$$

Hence,

$$h = \phi(T) \exp \left[- w(o)/kT \right] 2\pi a^3 g$$

Substituting the value of h in 10(A):

$$C_{Ki} = \frac{1}{kT} 2\pi a_i^3 g_{Ki} \exp \left(- \frac{w_{ki}(o)}{kT} \right) \quad (18)$$

Equation 18 can be successfully used to evaluate the Langmuir constants. Numerical integration of (17) will yield the value of g_{Ki} which may be subsequently used in (18) to obtain C_{Ki} .

EXPERIMENTAL PROGRAMME

Equipment

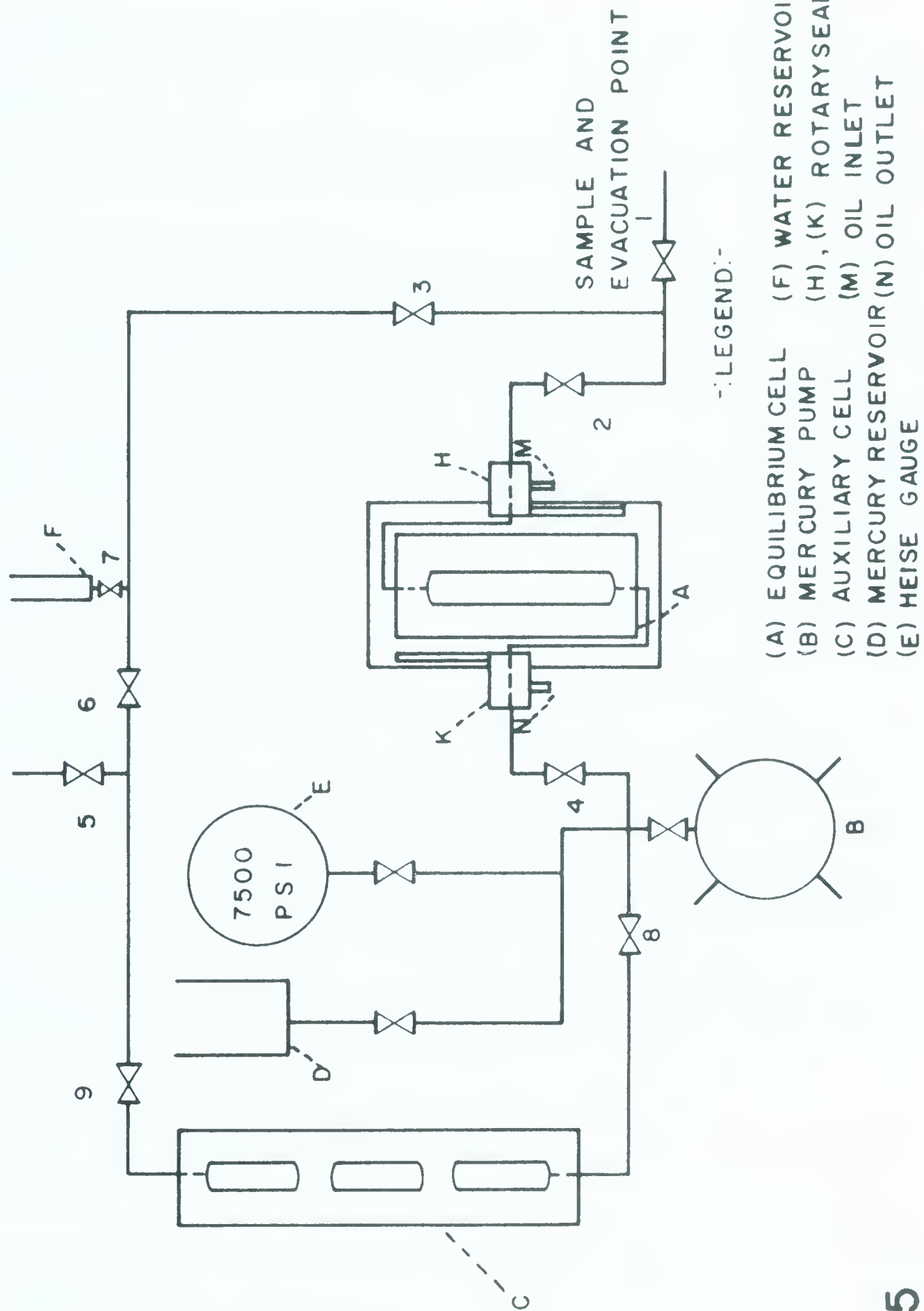
Equipment used in this investigation was similar to that used by earlier workers for the study of gas-hydrates and volumetric studies at the University of Alberta. The equilibrium cell used in this work was the same as that used by Snell⁽²¹⁾ for the study of gas-hydrates.

The main parts of the equipment are as follows:

- (1) Equilibrium cell
- (2) Mercury pump
- (3) Rotary seals
- (4) Constant temperature bath
- (5) Agitating mechanism

Equilibrium Cell

The equilibrium cell was a Penberthy liquid level gauge capable of withstanding 6000 psia at 250°F, with a test pressure of 9000 psia. The cell was constructed of type 316 stainless steel with sight glasses on both sides and had an approximate volume of 120 cc.



516

The cell was enclosed in an 8" O.D. lucite jacket with lucite discs and O-rings on both ends to make the seal. Both the ends of the cell were connected with aminco tubing, which rested in a bearing placed in rotary seals.

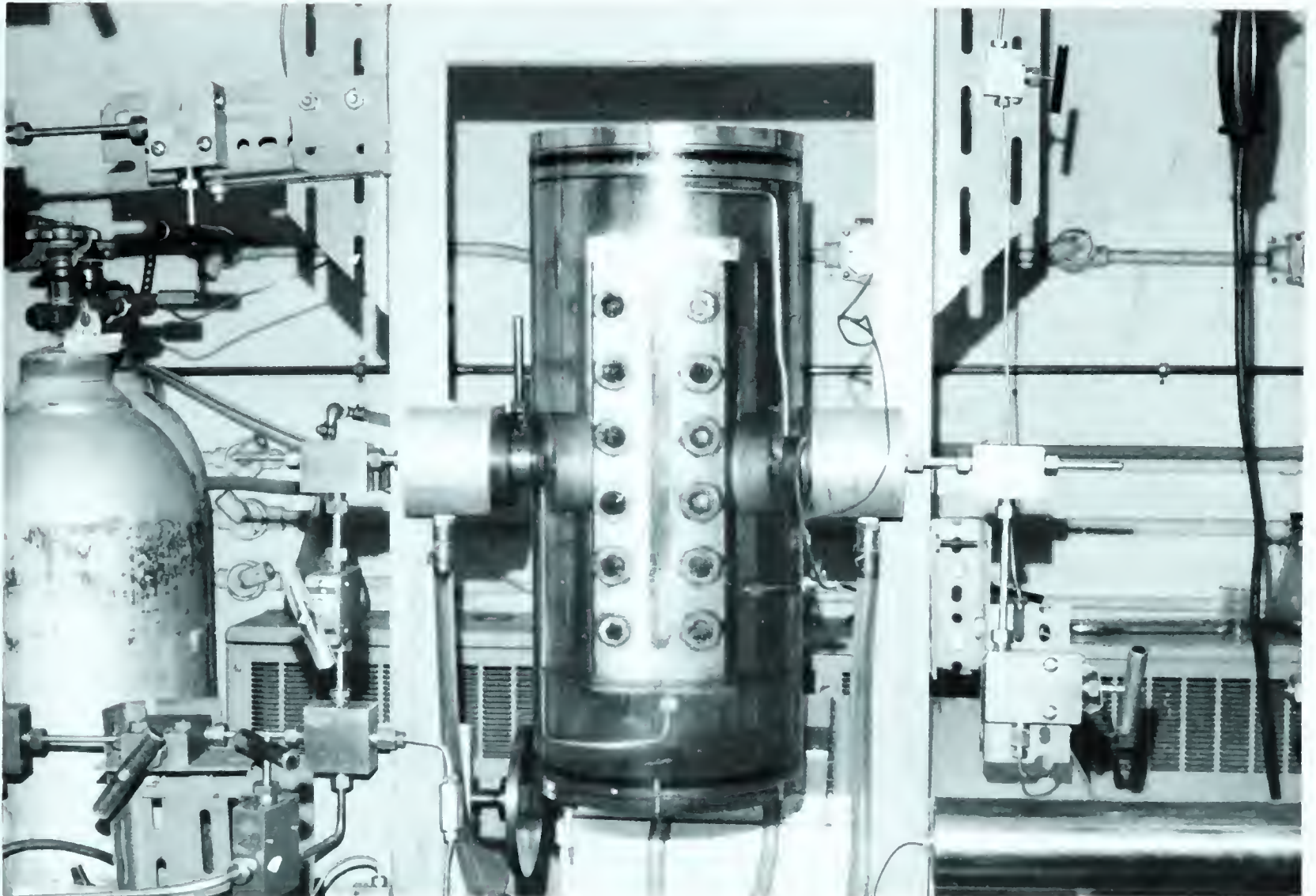
Two sight glasses, used on each side of the cell served as glass windows for visual observations of the phase behaviour, and were capable of withstanding 9000 psia at 100°F. Figure 8 shows the complete assembly of the equilibrium cell with the glasses.

Mercury Pump

A high pressure positive displacement pump, with a pressure rating of 8,000 psi and displacement volume of 265 cc. was used to raise or lower the pressure in the cell by injecting or withdrawing mercury. Graduations on the pump indicated the amount of mercury injected or withdrawn. Volumetric calibration of the cell was performed using the pump.

Rotary Seals

Rotary seals similar to those used by Snell⁽²¹⁾ were employed with great success to prevent the leakage of the charge during rocking of the cell. Details of the seals are given in



THE EQUILIBRIUM CELL

FIGURE 6

Figure 7. The Aminco tubes connecting the equilibrium cell were made to pass through the hollow brass shafts which rested in bearings in the aluminum housings. Synthetic rubber seals were used in the housings to prevent the leakage of the coolant. An Aminco tee with a $\frac{1}{2}$ " hole drilled through it was used to make the seal. The Aminco tube passed through this hole and rotated as an axle in bearing. The end of the Aminco tube was welded. A $\frac{1}{16}$ " hole was drilled through the side into the inside of the tubing for the introduction of the charge into the cell.

There was enough clearance between the tubing and the block so that mercury was around the tubing and the pressure therefore transmitted to the cell at all times. Teflon O-rings were tightened down by steel sleeves enclosed in Aminco nuts to make the seal.

Constant Temperature Bath

The contents of the equilibrium cell were maintained at a constant temperature by circulating varsol. Varsol was circulated through the lucite jacket around the cell using a centrifugal pump immersed in an insulated tank filled with varsol. A freon refrigeration unit and two heaters of 1000 watt and

500 watt capacities were employed. The temperature in the bath was controlled by an American Instrument Co. bimetallic strip controller. This controller was connected through a relay and transformer to the refrigerator. Temperature control was within $\pm 0.1^{\circ}\text{F}$.

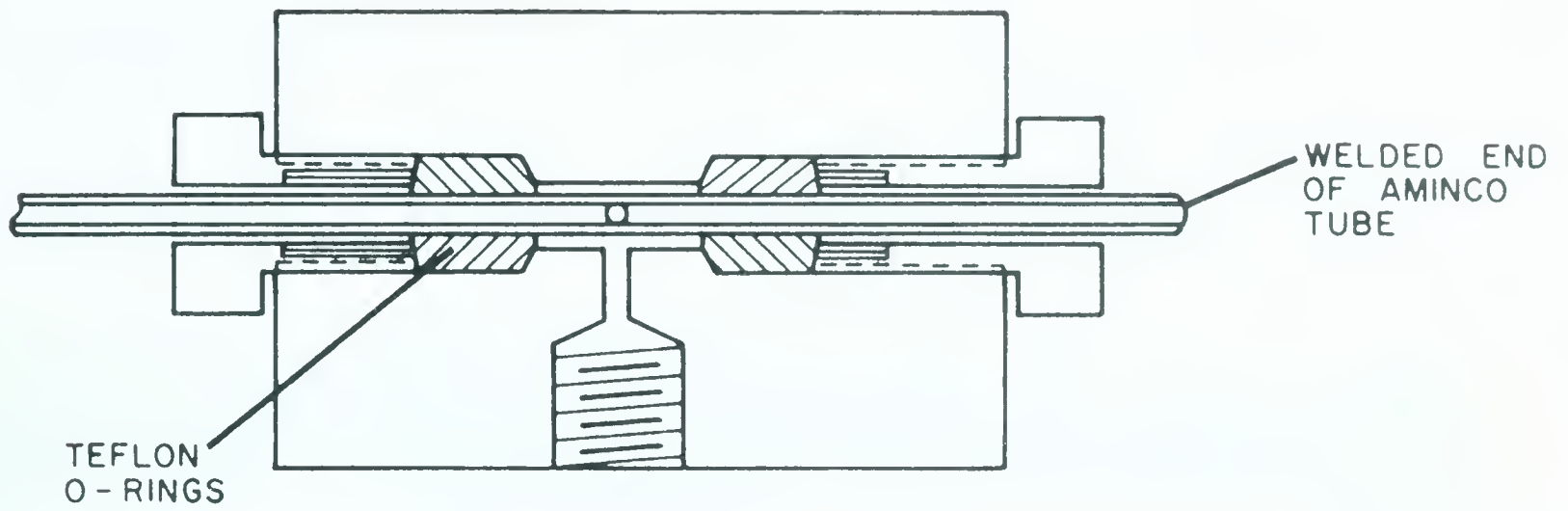
The temperature in the equilibrium cell was measured with the help of an iron-constantan thermocouple, inserted through the side of the cell.

Agitating Mechanism

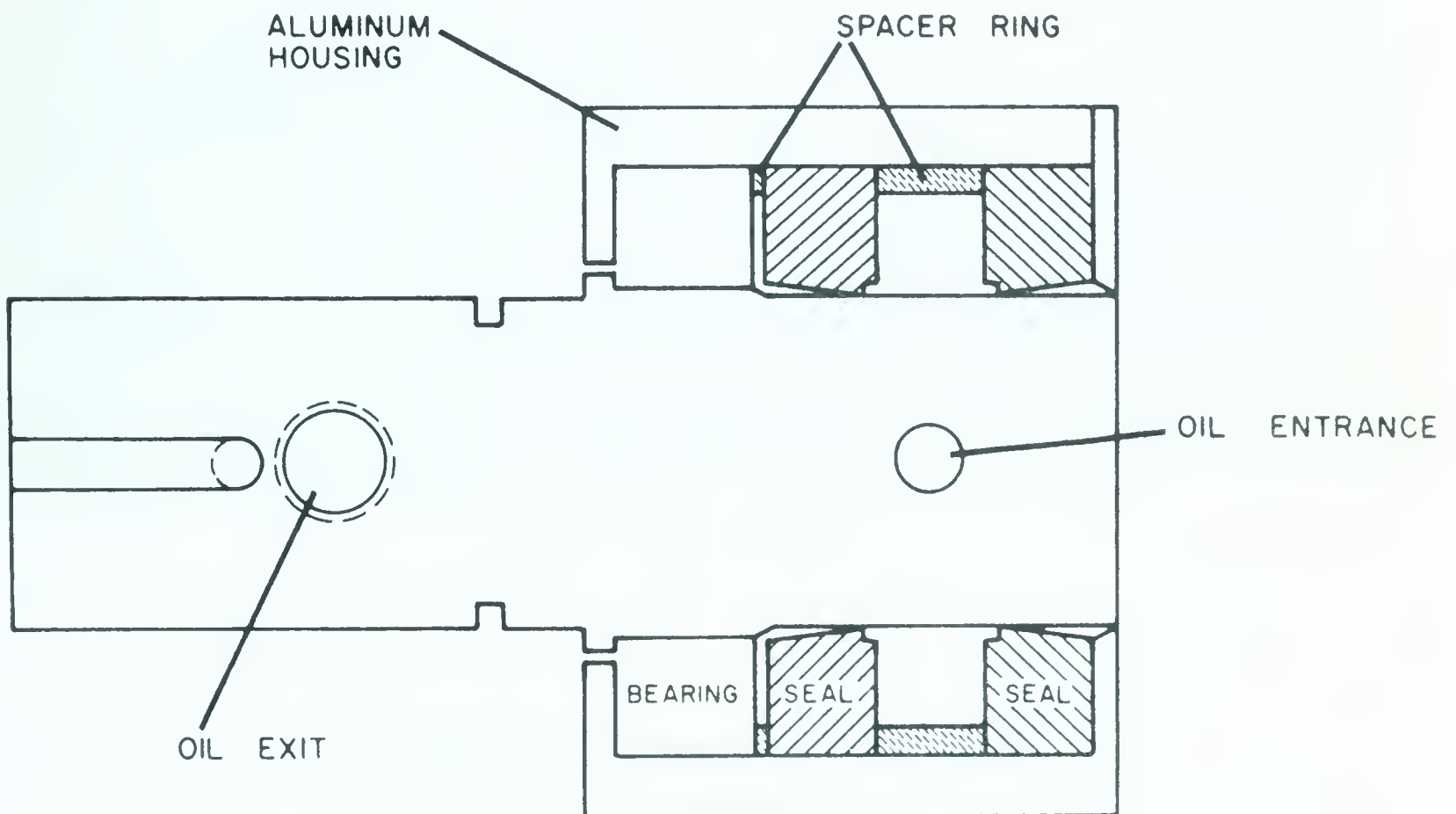
A 1/6 horse-power electric motor was employed to drive an eccentric which was connected to the cell through a connecting rod. To provide necessary agitation, the cell was rocked through a small arc of 30° - 35° when the contents of the cell moved back and forth.

Valves and Tubings

Aminco and Autoclave tubings were used in the experimental equipment. Aminco tubings supplied by American Instrument Company, with an inside diameter of 3/32" and a wall thickness of 1/8" were used. Both Aminco fittings and tubings were of type 304 stainless steel and rated at 30,000 psia at 100°F .

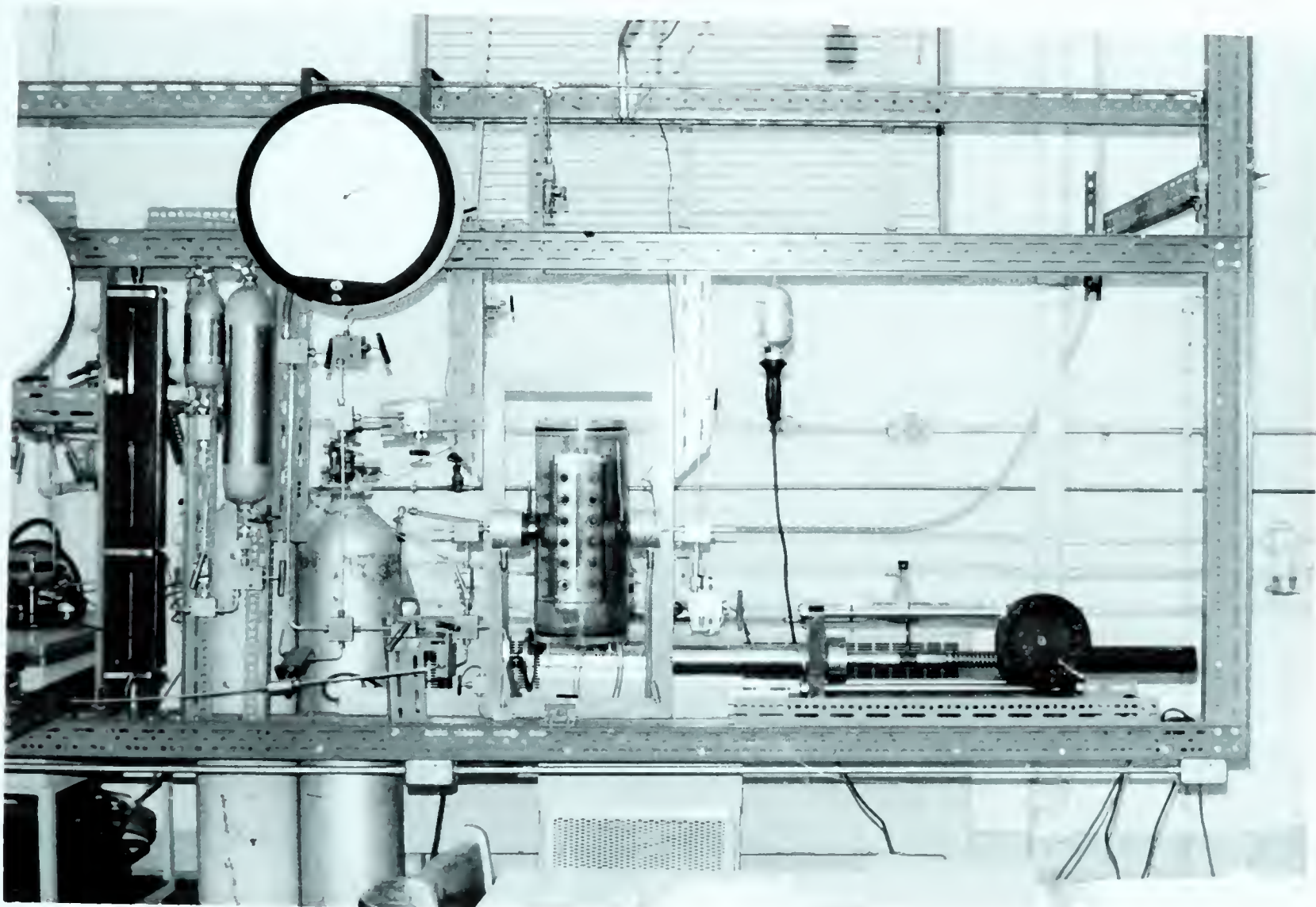


ROTARY SEAL



SWIVEL ASSEMBLY FOR EQUILIBRIUM CELL

FIG. 7



THE ASSEMBLY OF THE EQUIPMENT

FIGURE 8

Autoclave tubings, made by Autoclave Engineers Inc. had an outside diameter of 1/8" with a wall thickness of 1/32". The tubings and valves were rated for 15,000 psia at 100°F and were constructed of type 316 stainless steel.

The methane gas used in this investigation was obtained from the Matheson Company, with a specified purity of 99.8%. The nitrogen gas was obtained from the Liquid Carbonic Canadian Corporation Limited, with a specified purity of over 99.6%.

Experimental Technique

Figure 5 is the schematic diagram of the assembly of equipment. Initially the equilibrium cell was filled with mercury with the help of the mercury pump. Keeping valves 2 and 3 open, some mercury was collected in the trap, so as to make sure that the tubing was filled with mercury up to valve 2. Valve 2 was then closed and the line from valve 6 to valve 1 was evacuated (keeping valve 6 closed). Valve 1 was closed and valve 7 was opened for the introduction of water into the cell. Valves 2 and 4 were opened, and by slowly withdrawing mercury from the equilibrium cell, water was introduced. Approximately 15 - 20 cc of water were taken each time. Valves 7 and 2 were closed and the line connecting the gas cylinder

and the cell was evacuated. Valve 1 was then closed and the desired amount of gas was taken into the equilibrium cell. The same process was repeated to introduce another gas into the cell to make the desired composition of the gaseous mixture. The gas from a cylinder with a lower pressure was always taken in first. Any predetermined mixture of the gases could be prepared by adjusting the initial pressure of the pure gas samples. The charge thus taken into the cell was allowed to mix completely by rocking the cell for 15 - 20 minutes. Special care was taken to see that valves 2 and 4 were kept closed during the experiment. Later a small sample of this charge was chromatographically analysed.

Technique for the Determination of Initial Hydrate-Forming

Conditions

Once the composition is fixed, a ternary system behaves exactly like a binary system as regards its initial hydrate-forming conditions. Therefore, the procedure followed for the determination of initial hydrate forming conditions for a ternary system with a fixed composition is exactly the same as that for a binary system. At a particular temperature the equilibrium pressure of the three phases can be approximately

determined. The contents of the cell were kept at a pressure slightly above this predetermined pressure and the system was subjected to supercooling of 8°F to 12°F . The cell was allowed to rock for 30 to 60 minutes, when the hydrate phase usually appeared. Formation of hydrate was accompanied with a drop in pressure. The temperature of the system was slowly raised to decompose all but a few crystals of hydrates. With the rise in temperature, the pressure also rose slowly due to decomposition of the hydrate. When very few crystals of the hydrate were seen adhering to the glass wall, the temperature and pressure were noted. The final pressure of the system was very close to the initial pressure. At this stage, lowering the temperature by half a degree to one degree was enough to obtain sufficient hydrate crystals. The pressure of the system was raised and the same procedure was repeated to get another point.

Technique for the Determination of Pressure - Composition

Diagram for $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ System

In a ternary system, the composition of the two phases, gas and hydrate, in equilibrium with the water phase, will depend on the pressure and temperature of the system. The

method followed to obtain data on this aspect of the three phase equilibrium is briefly described below.

Initially the charge consisting of water and desired composition of the gas was taken in the cell as described earlier. The charge was compressed to a pressure which was 25% - 30% greater than that needed for initial hydrate forming conditions. The temperature was set at the desired value and after closing valve 2, the cell was allowed to rock for four to six hours. Special care was taken to see that the plunger of the mercury pump was maintained in its position throughout the experiment. In the end when equilibrium between the phases was established the pressure was constant. The drop in pressure was a direct function of the amount of hydrate crystals formed. After noting the final pressure the sample of the gaseous phase was analysed chromatographically.

Hydrate composition was determined by direct analysis as well as by calculations. First the gas from the equilibrium cell was isobarically transferred to the auxiliary cell. Hydrate crystals were retained at the top. Drops of water and mercury falling into the auxiliary cell indicated the complete transfer of gas from the equilibrium cell to the auxiliary cell. Valve 2 was closed and the lines connecting the equilibrium cell

to the auxiliary cell were evacuated to prevent contamination of the sample with the traces of the gas remaining in the line. The pressure in the cell was decreased and the temperature was raised to decompose the hydrate. Later, the sample of the gas generated on decomposition of the hydrate was chromatographically analysed. An indirect method of determining the hydrate composition from the gas-phase compositions and pressure data is given elsewhere.

The procedure described above was repeated to cover the range of pressures in which the two gases form hydrates.

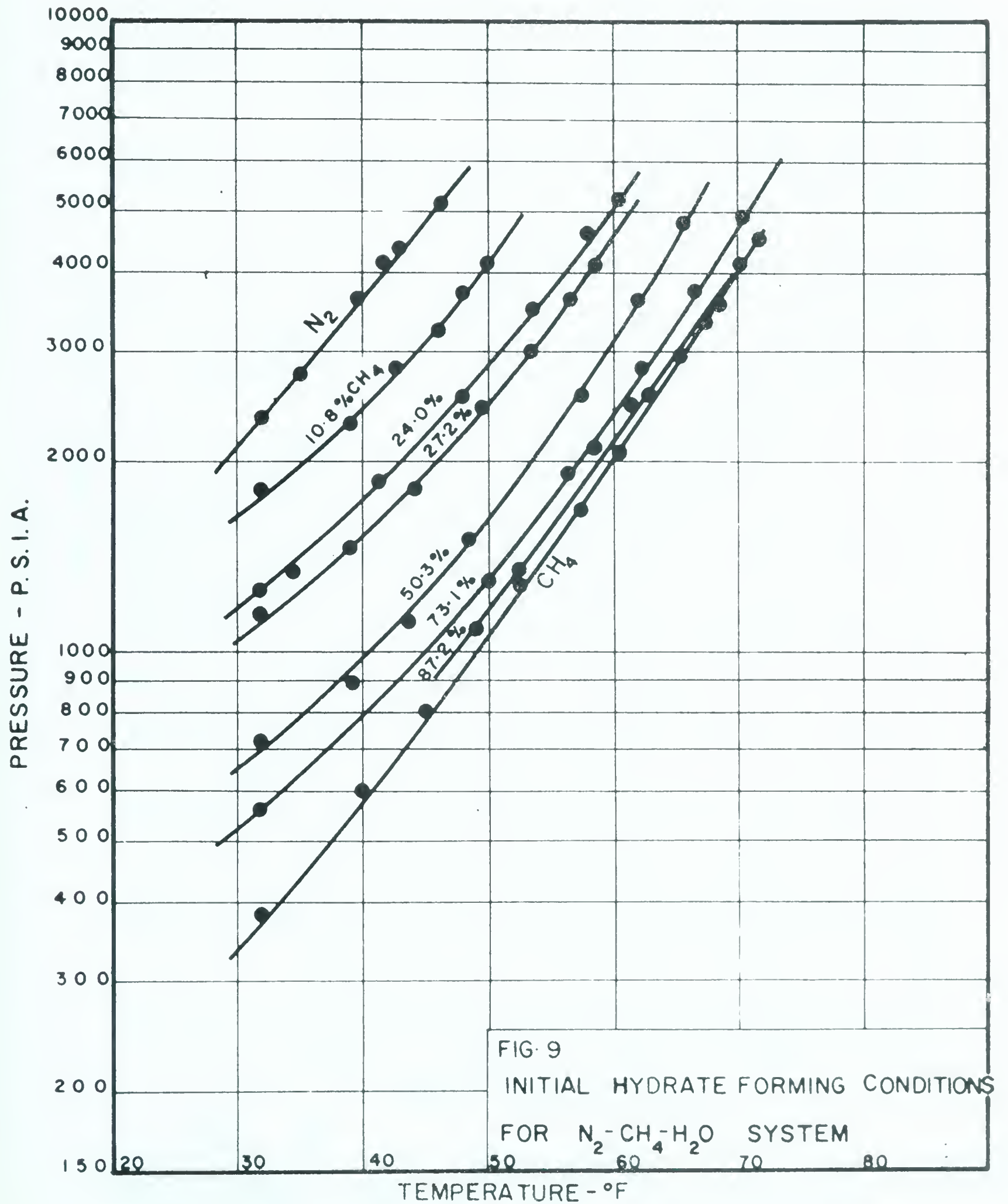
EXPERIMENTAL RESULTS

Initial Hydrate-Forming Conditions

Six mixtures of nitrogen and methane were studied to obtain data on equilibrium pressures at various temperatures for the three phase-HLG-equilibrium. The temperature and pressure ranged from 32°F to 72°F, and 300 psia to 5,100 psia respectively.

The pressure temperature data are presented in Table 1. The pressure temperature data for hydrates of pure nitrogen and methane were also obtained and found to agree very well with the data of Van Cleeff and Diepen⁽²⁷⁾, Otto⁽¹³⁾, and Snell⁽²¹⁾.

Figure 9 represents the hydrate forming conditions of pure nitrogen, pure methane and mixtures of nitrogen and methane. The pressure temperature loci in this figure show a general trend which one might expect from the published data on other ternary systems. Close observation of the family of plots indicates the interesting fact that the slope of the pressure-temperature curves increases with the rise in temperature and it increases at a faster rate for a gaseous mixture with lower nitrogen content. At a certain equilibrium pressure, the



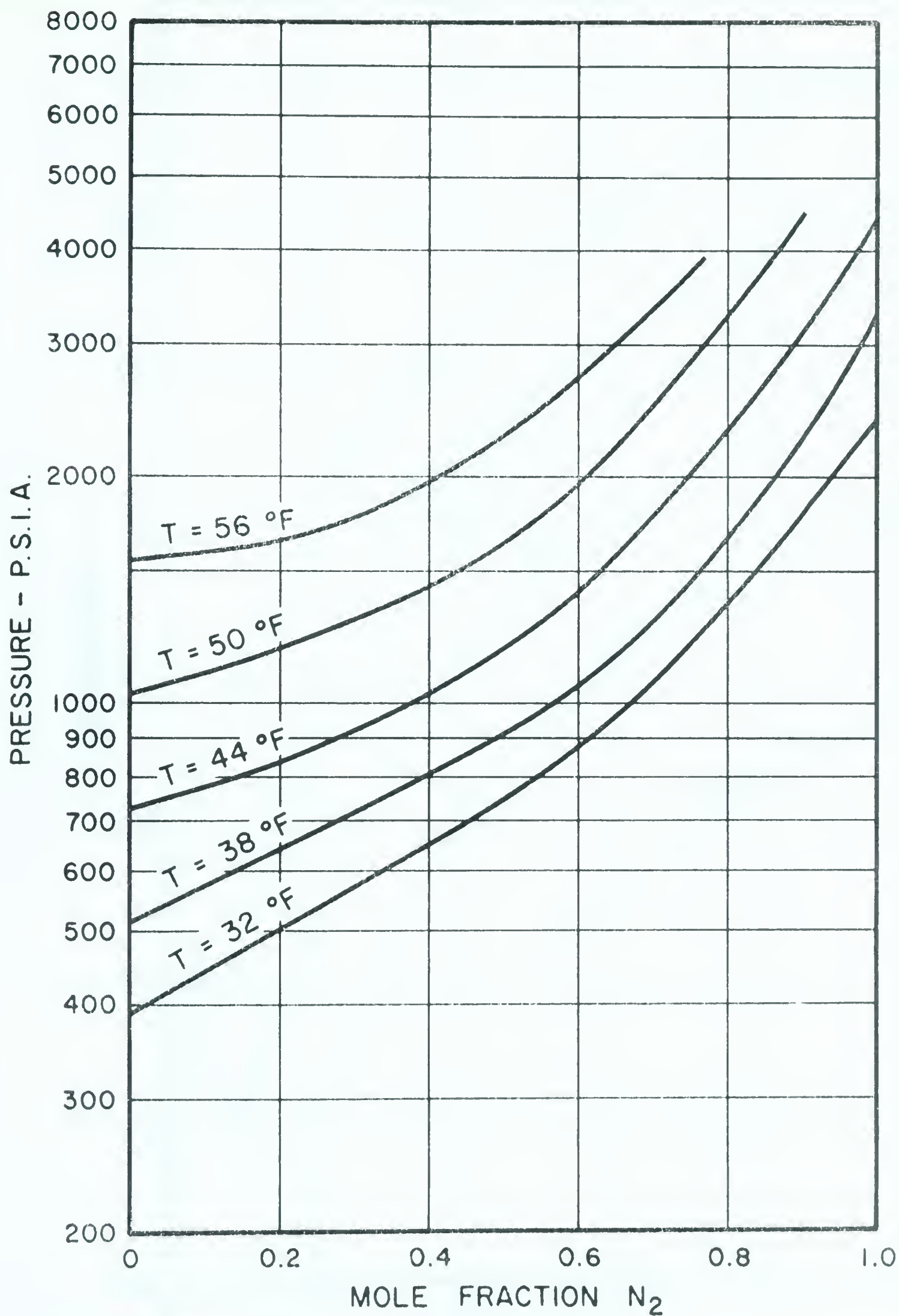


FIG. 10
ISOTHERMAL DATA ON INITIAL HYDRATE FORMING
CONDITIONS FOR $N_2-CH_4-H_2O$ SYSTEM

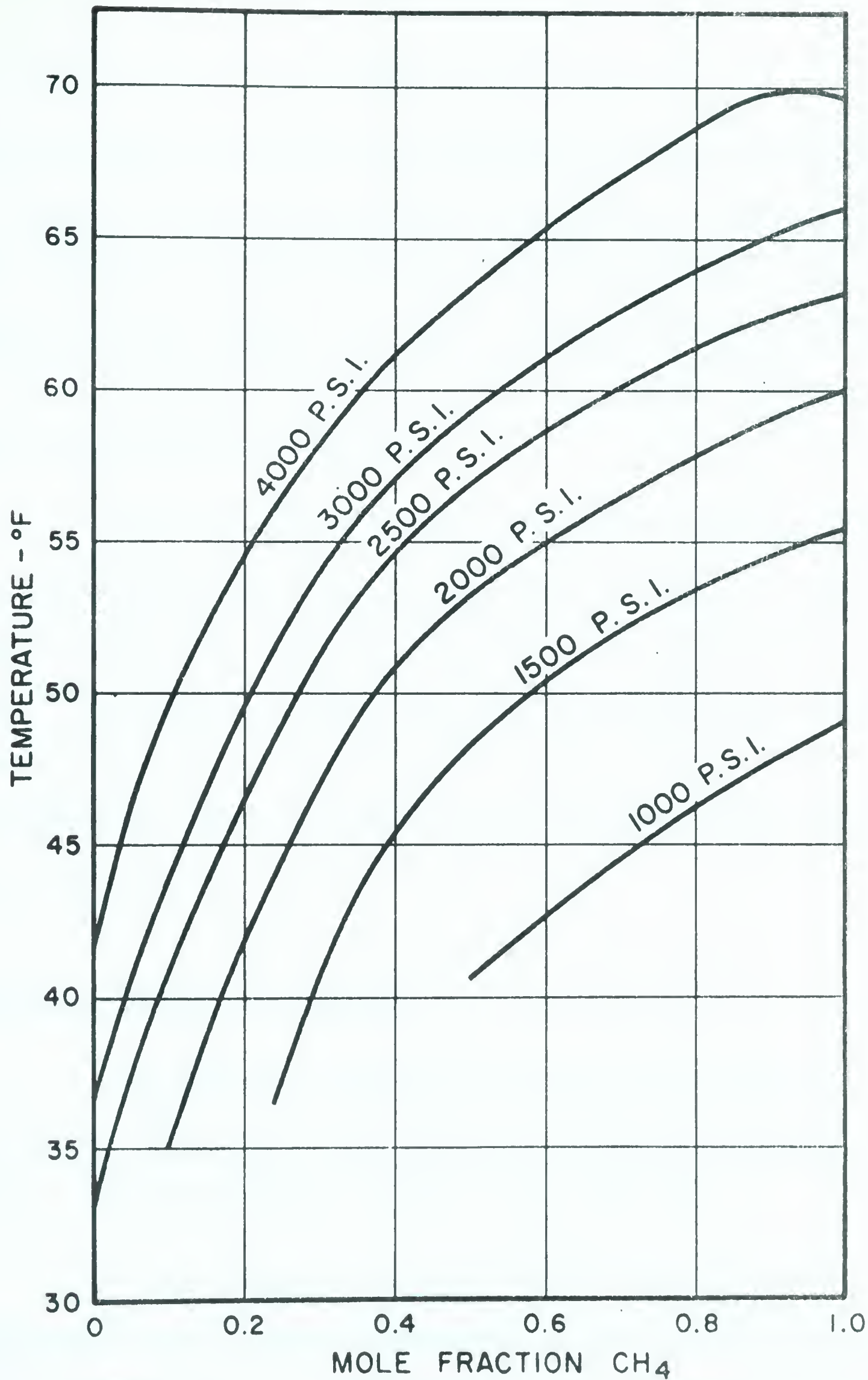


FIG. II
ISOBARIC DATA ON INITIAL HYDRATE FORMING
CONDITIONS OF $N_2-CH_4-H_2O$ SYSTEM

rate of change of equilibrium temperature with the percentage of nitrogen in gas containing more than 50% N_2 is higher than that existing for gases containing less than 50% N_2 . Consequently pressure temperature curves for gaseous mixtures with a fixed difference in nitrogen content are closely spaced as the nitrogen content decreases.

It is interesting to note that the equilibrium pressures for the mixture with 87.1% CH_4 are lower than those for pure methane above $67^{\circ}F$. A similar phenomenon was observed by Otto⁽¹³⁾ and Snell⁽²¹⁾ during the investigation of CH_4 - C_2H_4 - H_2O system. Equilibrium pressures for mixtures of methane and ethylene were lower than those for pure ethylene above a certain temperature.

Pressure Composition Diagrams

The pressure composition diagrams for N_2 - CH_4 - H_2O systems at $32^{\circ}F$, $39.7^{\circ}F$, and $44^{\circ}F$ were determined experimentally. They are shown in Figures 12, 13, and 14A.

It is apparent from the diagrams that the points indicating the gas-phase compositions in the diagrams do not show as much deviation from the mean curve as the points indicating the hydrate phase compositions. This discrepancy for the

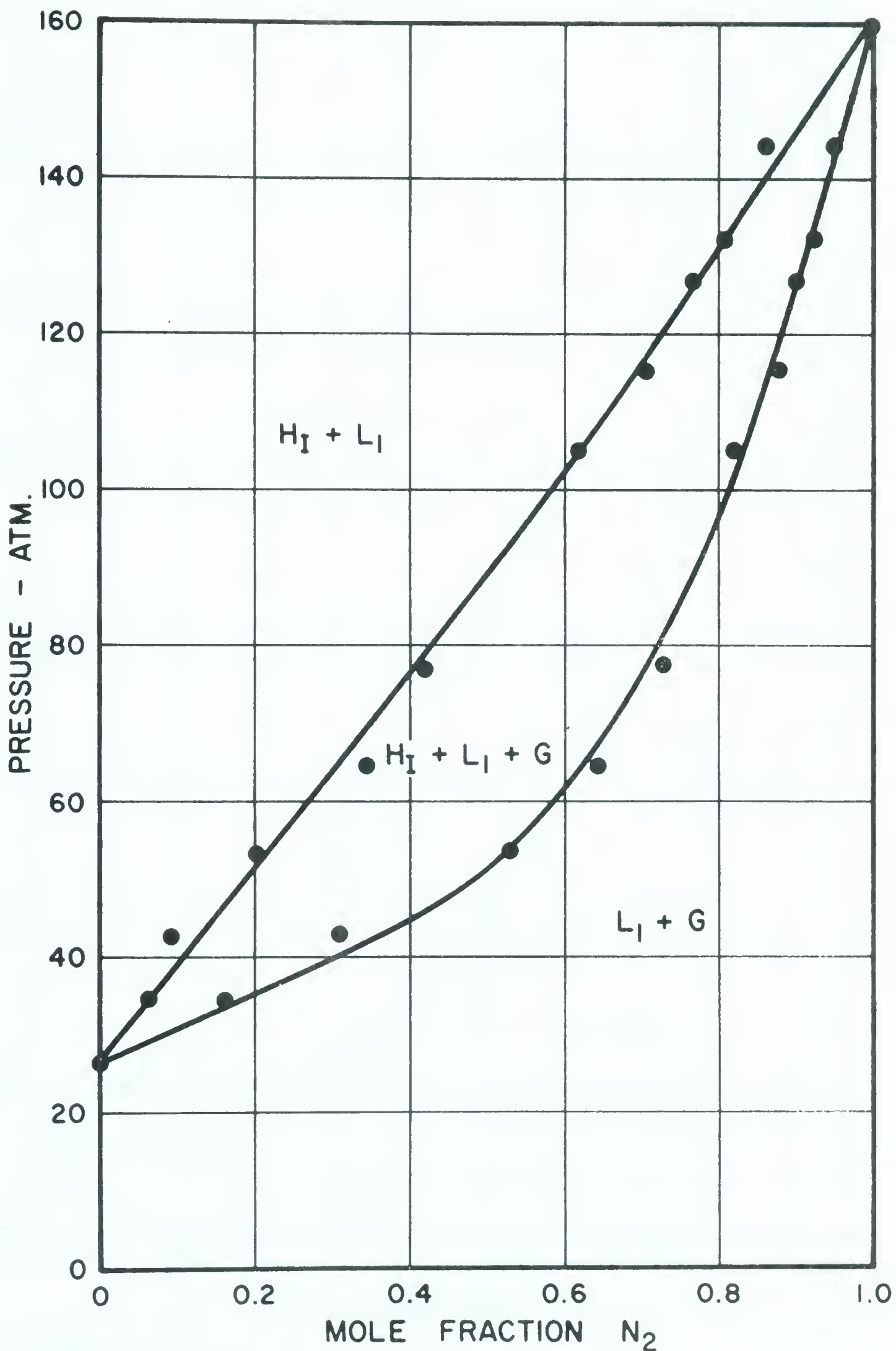


FIG. 12

PRESSURE COMPOSITION DIAGRAM FOR
 $N_2 - CH_4 - H_2O$ SYSTEM AT 32 °F

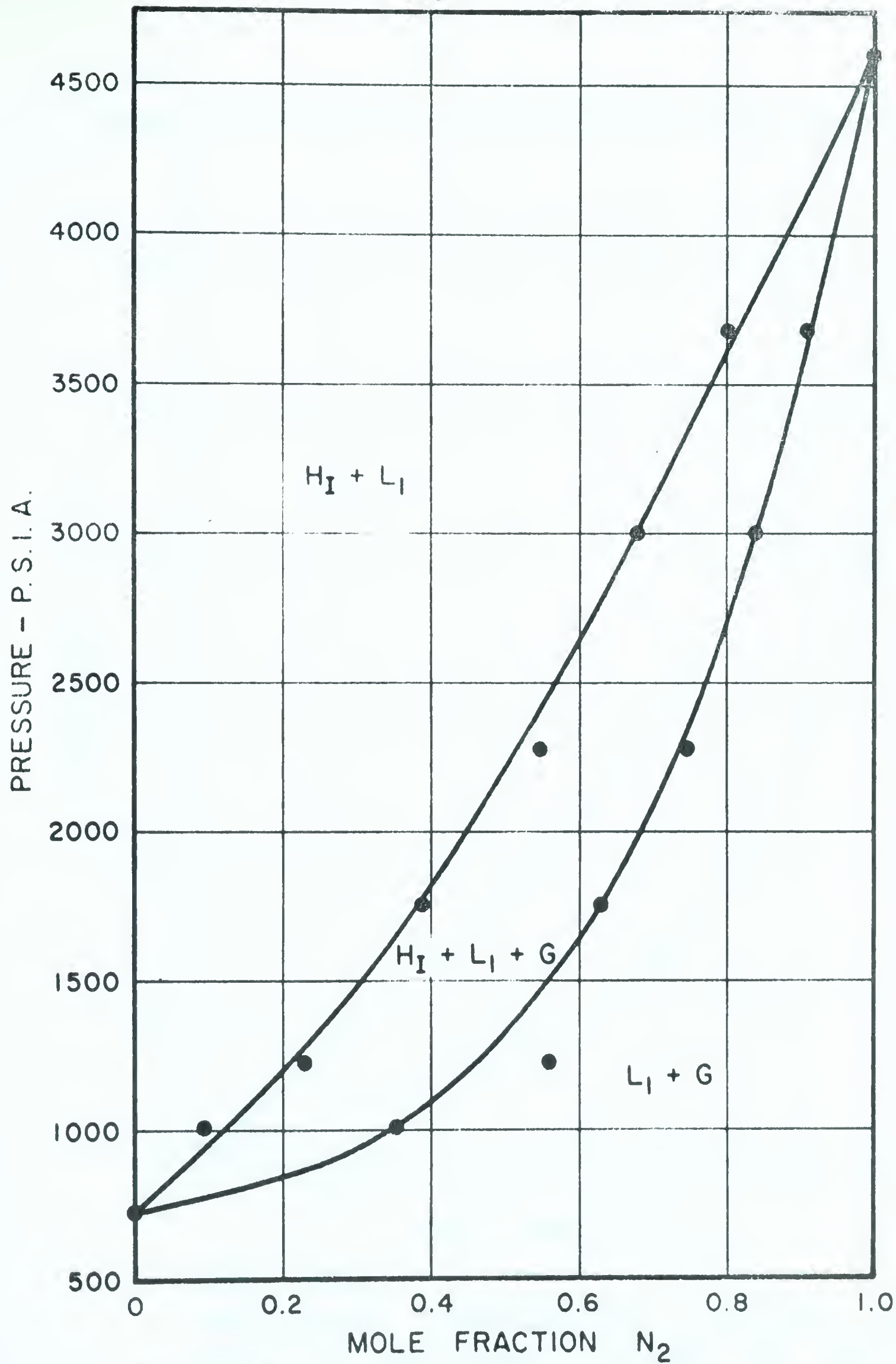


FIG. 13

PRESSURE COMPOSITION DIAGRAM FOR
 $N_2 - CH_4 - H_2O$ SYSTEM AT 44 °F

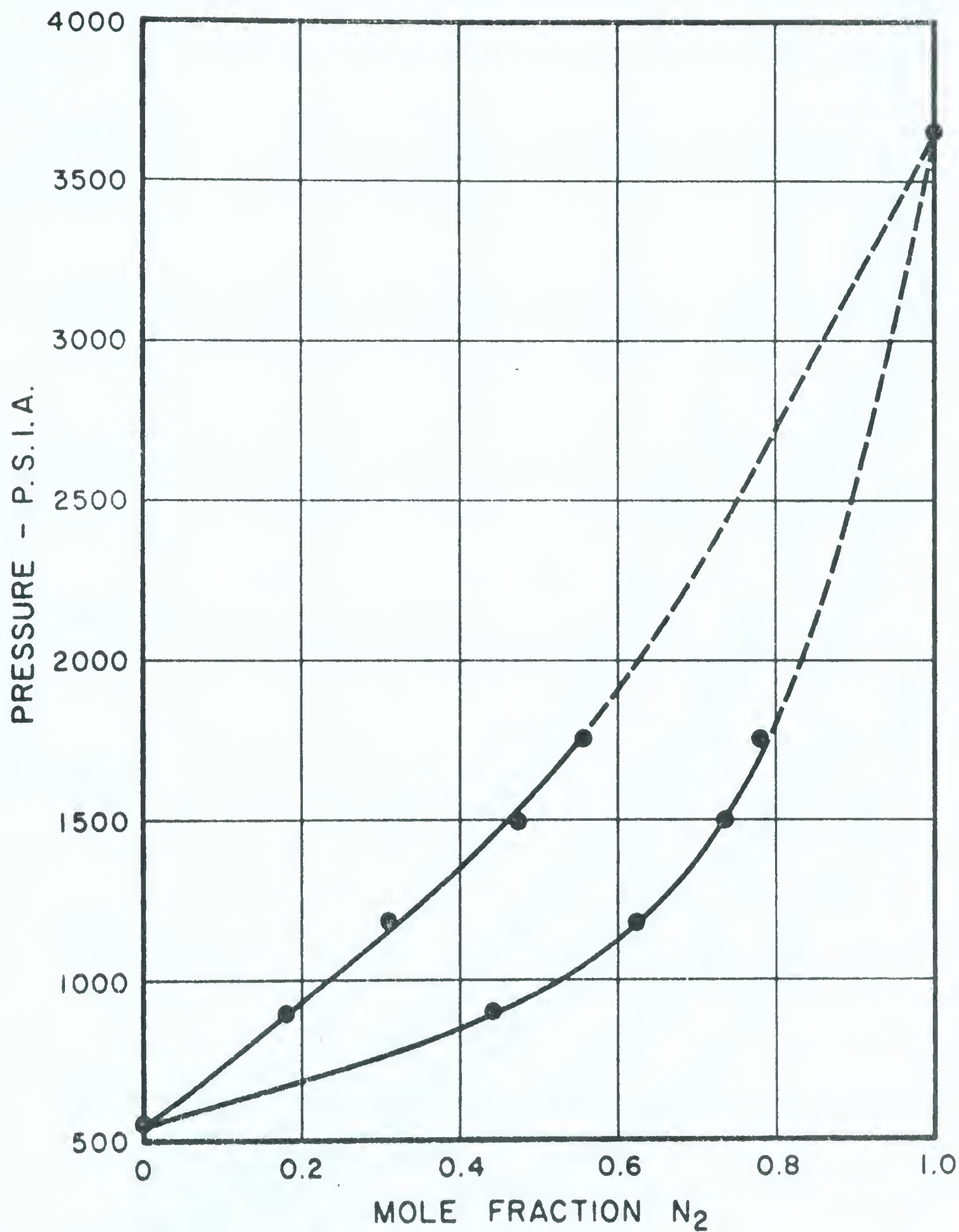


FIG. 14A

PRESSURE COMPOSITION DIAGRAM FOR
THE N_2 - CH_4 - H_2O SYSTEM AT 39.7°F

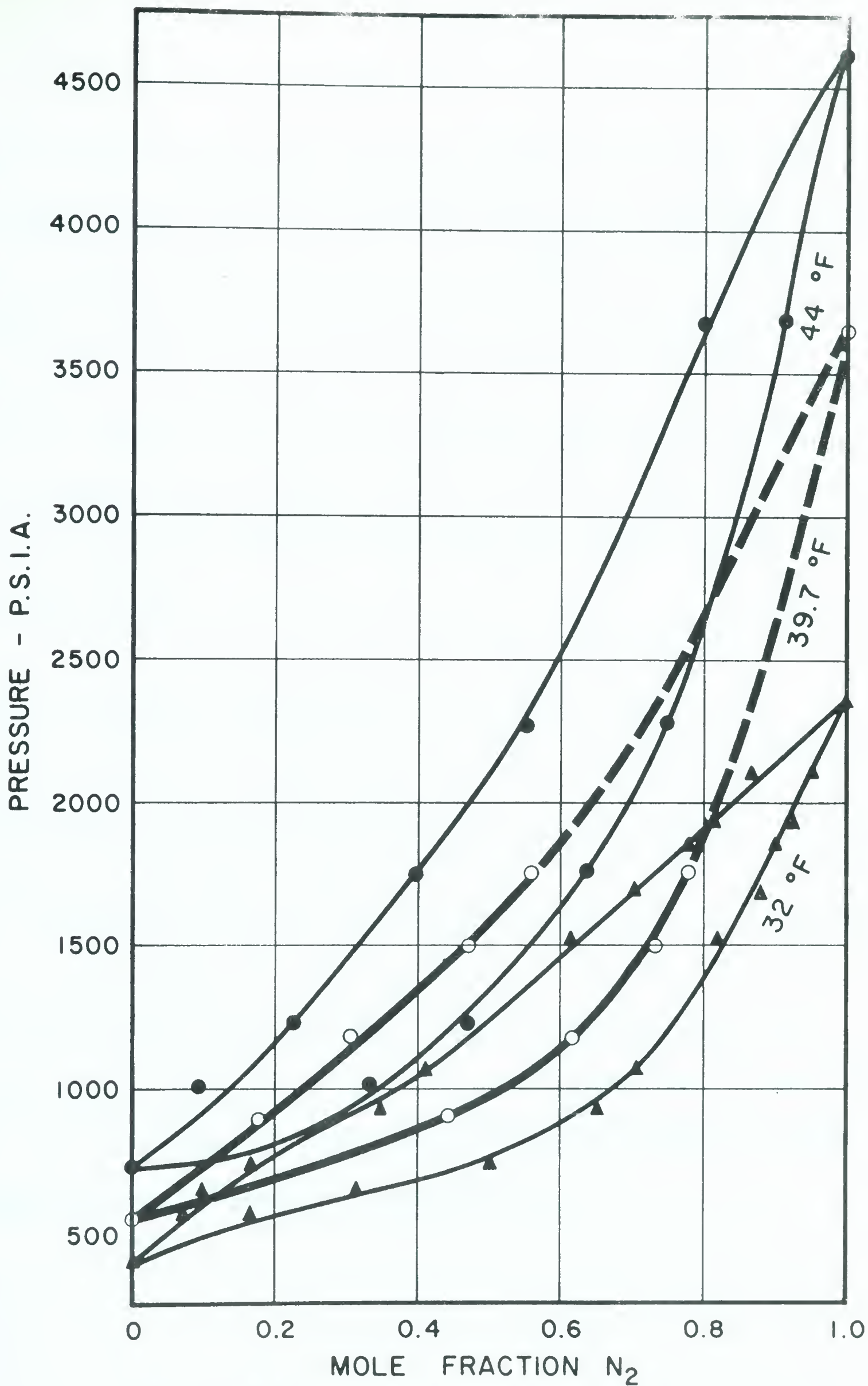


FIG. 14 B

PRESSURE COMPOSITION DIAGRAMS FOR
THE $N_2-CH_4-H_2O$ SYSTEM

hydrate branch may be attributed to the fact that during the transfer of gas from the equilibrium cell to the auxiliary cell, truly isobaric conditions were not maintained and the hydrate composition might have changed due to disturbed equilibrium conditions. The likelihood of occlusion of gas in the hydrate crystals appears to be another plausible explanation for this discrepancy. The calculated values of hydrate compositions do not show very much deviation from the experimental values. In the worst cases the deviation is less than 15%. It is interesting to note that in most of the cases the calculated values of hydrate compositions give higher methane concentration. As the indirect method for the calculation of hydrate composition as described in Appendix B is very sensitive to the composition and compressibility factors of the gaseous mixtures, the experimental values of the hydrate compositions were thought to be more reliable and have been used in the above diagrams. Compressibility factors used in these calculations were computed from an equation of state and not obtained experimentally. The indirect method for the determination of the hydrate phase composition is illustrated in Appendix B.

THEORETICAL CALCULATIONS

Prediction of Pressure - Composition Diagrams

One of the objectives of this investigation was to apply the solid solution theory to the experimental results. It was decided to obtain the pressure-composition diagrams at 32°F for three ternary systems, N₂-CH₄-H₂O, CH₄-C₂H₆-H₂O and CH₄-C₂H₄-H₂O.

The underlying assumptions and the various steps involved in these calculations are given below.

At equilibrium, three phases - hydrate, water and gas coexist. For a hydrate to be stable with respect to modification of water, (ice or liquid water);

$$\mu_Q \leq \mu_Q^\alpha \quad (19)$$

writing
$$\Delta\mu_{(T,P)} = \mu_Q^\beta - \mu_Q^\alpha \quad (20)$$

for the difference between the chemical potentials of the two modifications, which is a function of temperature and total pressure, and substitution of Equation 13 into Equation 20 above, gives,

$$\sum \gamma_i \ln (1 + \sum_K C_{Ki} P_K) \geq \Delta\mu/RT \quad (21)$$

For an equilibrium hydrate the sign of equality in the Equation 21 holds. Nitrogen and methane, being small molecules relative to C_3H_8 and SF_6 occupy both the cavities of Structure I and the Equation 21 will have the following form for the $N_2-CH_4-H_2O$ system.

$$\gamma_1 \ln (1 + C_{M_1} \cdot x \cdot p + C_{N_1} \cdot \frac{1}{1-x \cdot p}) + \gamma_2 \ln (1 + C_{M_2} \cdot x \cdot p + C_{N_2} \cdot \frac{1}{1-x \cdot p}) = \frac{\Delta\mu}{RT} \quad (22)$$

The values of the various constants needed in the above equation are as follows (29):

$$\begin{aligned} \gamma_1 &= 1/23 \\ \gamma_2 &= 3/23 \\ \Delta\mu &= 0.167 \text{ kcal./mol} \end{aligned}$$

Langmuir Constants

	<u>Nitrogen</u>	<u>Methane</u>	<u>Ethane</u>	<u>Ethylene</u>
C_1	0.0474	0.2361	4.67	2.185
C_2	0.0606	0.2685	4.350	14.57

Langmuir constants were evaluated from the data on fractional occupation and equilibrium pressures reported by Van der Waals and Platteeuw⁽³⁰⁾.

Writing

$$C_{M_1} \cdot x + C_{N_1} \cdot (1 - x) = D_1$$

and $C_{M_2} \cdot x + C_{N_2} \cdot (1 - x) = D_2$

Equation 22 takes the following form,

$$(1 + D_1 P) (1 + D_2 P)^3 = e^{23(\Delta\mu/RT)} \quad (23)$$

On expanding,

$$1 + (3 D_2 P + D_1 P) + 3 D_2^2 P^2 + 3 D_1 D_2 P^2 + D_2^3 P^3 + 3 D_1 D_2^2 P^3 + D_1 D_2^3 P^4 = e^{23(\Delta\mu/RT)}$$

Writing

$$(a) \quad \frac{3 D_2 + D_1}{D_1 \cdot D_2^3} = 4 C$$

$$(b) \quad \frac{D_2^3 = 3 D_1 D_2^2}{D_1 \cdot D_2^3} = 4 a$$

$$(c) \quad \frac{3 D_2^2 + 3 D_1 D_2}{D_1 \cdot D_2^3} = 6 b$$

and (d) $\frac{1 - e^{23(\Delta\mu/RT)}}{D_1 \cdot D_2^3} = d$

Substituting these values in Equation 23, the following quartic equation is obtained

$$P^4 + 4 a P^3 + 6 b P^2 + 4 P c + d = 0 \quad (24)$$

Roots of the above equation are⁽¹⁶⁾,

$$R_1 = -a + \sqrt{u} + \sqrt{v + \sqrt{w}}$$

$$R_2 = -a + \sqrt{u} - \sqrt{v + \sqrt{w}}$$

$$R_3 = -a - \sqrt{u} + \sqrt{v - \sqrt{w}}$$

$$R_4 = -a - \sqrt{u} - \sqrt{v - \sqrt{w}}$$

where

$$u = g + 1, v = 2g - 1, w = 4u^2 + 3k - 12gl$$

$$g = a^2 - b, h = b^3 + c^2 - 2abc + dg, k = 4/3 ac - b^2 - d/3$$

$$l = 1/2 (h + \sqrt{h^2 + k^3})^{1/3} + 1/2 (h - \sqrt{h^2 + k^3})^{1/3}$$

Evaluation of the roots R_1, R_2, R_3 and R_4 was undertaken by writing a programme for the computer IBM 1620.

The method illustrated above gives the direct solution of Equation 24 without going into trial and error procedures.

Out of the four roots only one of them gives the desired value of the equilibrium pressure for a certain gas phase composition.

Composition of the hydrate phase was computed from the following equations:

$$x' = \frac{\sum_i \gamma_i \cdot y_{Ki}}{\sum_{K,i} \gamma_i \cdot y_{Ki}} \quad (25)$$

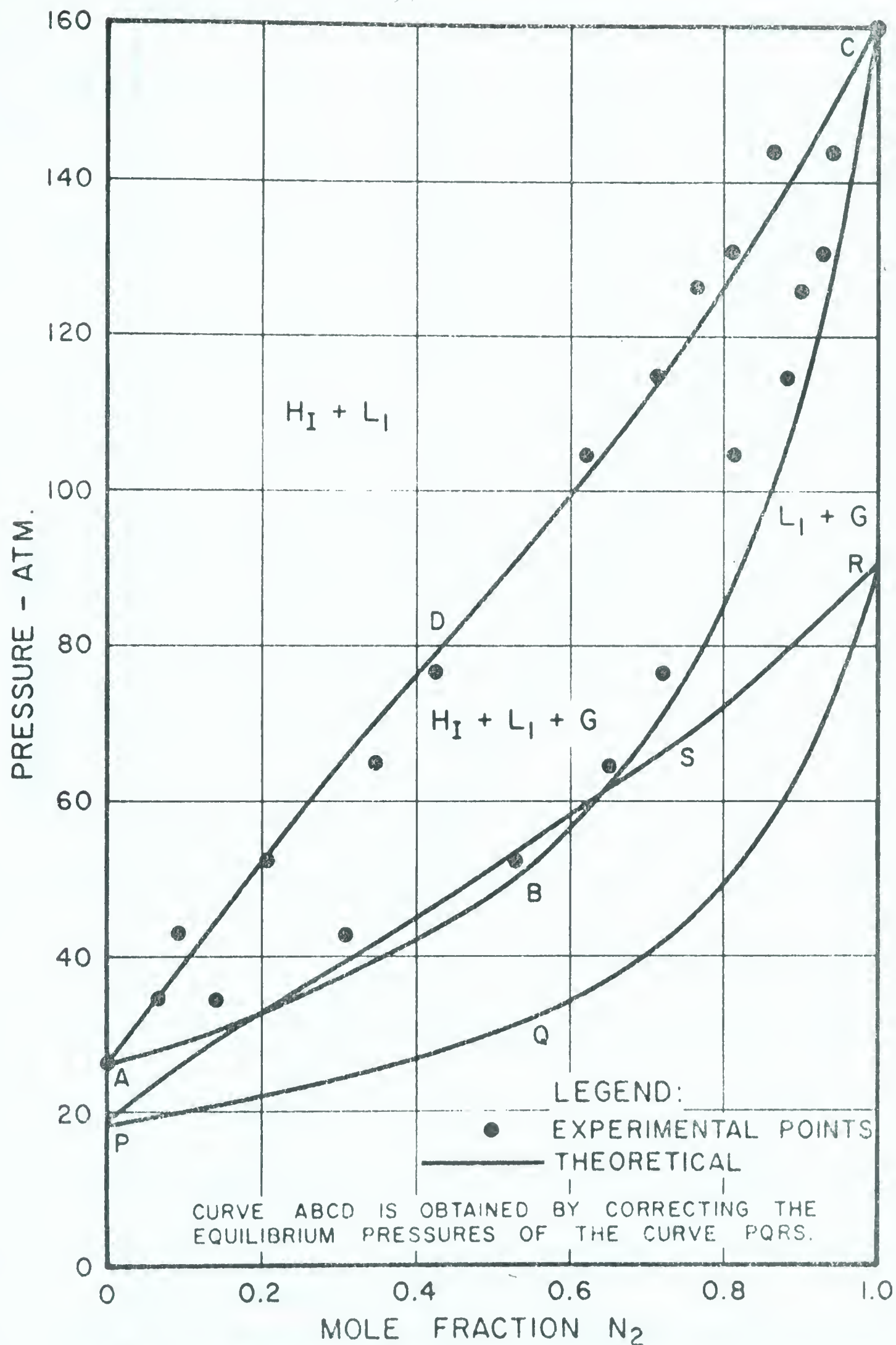


FIG. 14
 PRESSURE COMPOSITION DIAGRAM FOR
 $N_2 - CH_4 - H_2O$ SYSTEM AT 32 °F

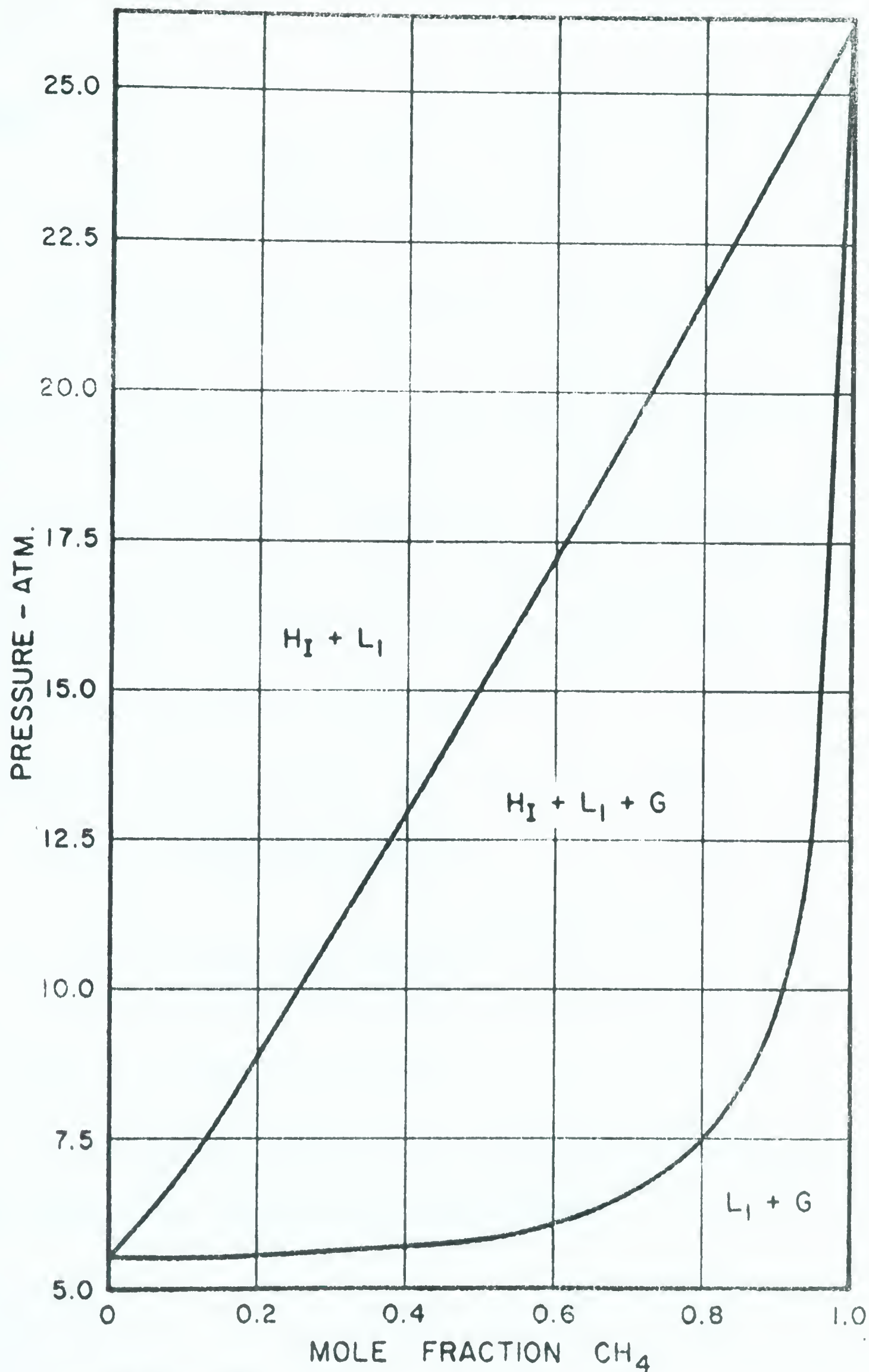


FIG. 16

PRESSURE COMPOSITION DIAGRAM FOR
 CH_4 - C_2H_4 - H_2O SYSTEM AT 32°F

where

$$Y_{Ki} = \frac{C_{Ki} \cdot P_K}{1 + \sum_K \gamma_i \cdot Y_{Ki}} \quad (26)$$

Theoretically predicted pressure composition diagrams for the three ternary systems, N_2 - CH_4 - H_2O , CH_4 - C_2H_6 - H_2O and CH_4 - C_2H_4 - H_2O are given in Figure 14, 15, and 16 respectively. Theoretically predicted diagrams have the corrected values of pressures as an ordinate. Experimental values of pressures are higher for all the gases. This is particularly true for N_2 , C_2H_4 and C_2H_6 . Theoretically predicted values of equilibrium pressures were corrected as follows,

$$P_{corrected} = P_{theoretical} (r_1 \cdot x + r_2 (1 - x))$$

$$r_1 = \frac{(P_A)_{experimental}}{(P_A)_{theoretical}}$$

$$r_2 = \frac{(P_B)_{experimental}}{(P_B)_{theoretical}}$$

and x = Mole fraction of A

r_1 , r_2 were evaluated at the temperature at which pressure composition diagrams were investigated.

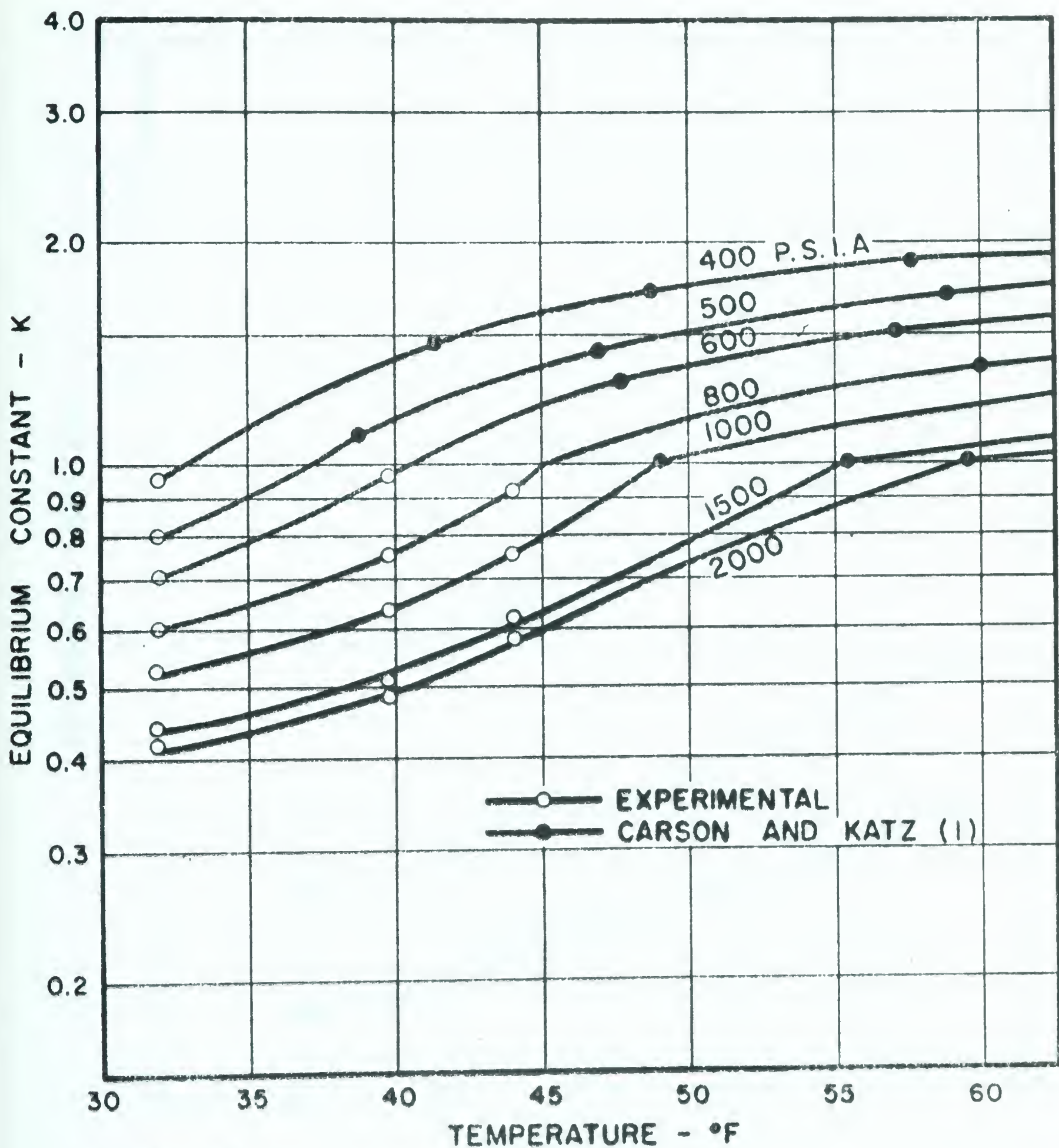


FIG. 17
EQUILIBRIUM CONSTANTS FOR METHANE

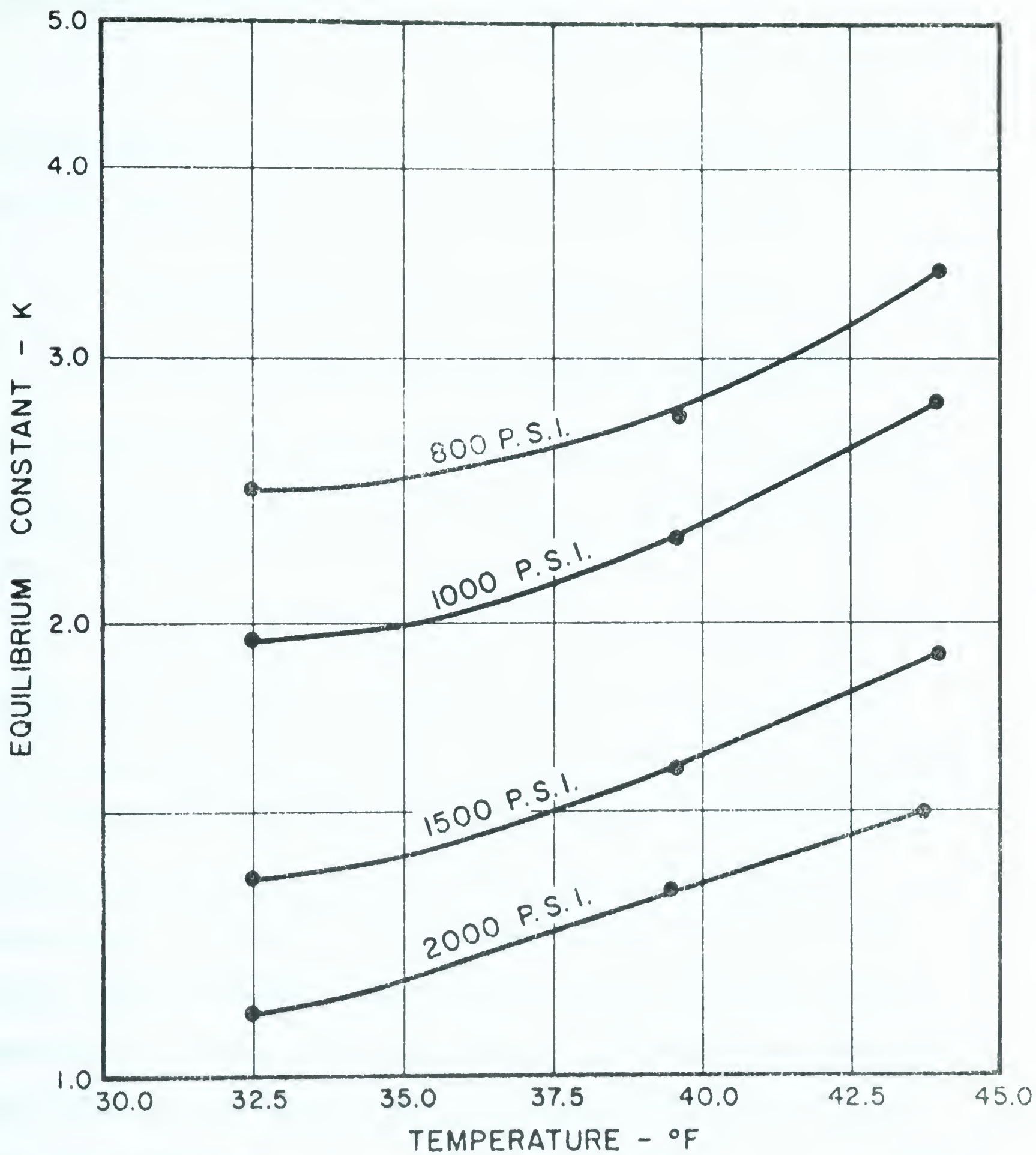


FIG. 18
EQUILIBRIUM CONSTANTS FOR N₂

Evaluation of the Equilibrium Constants

As stated earlier, Wilcox, Carson and Katz were the first to propose a solid-solution theory and develop the concept of solid-vapour equilibrium constants for gas hydrates.

The equilibrium constant has been defined as,

$$k_{v-s} = y/x = \frac{\text{Mole fraction of gas in vapour phase}}{\text{Mole fraction of gas in hydrate phase}}$$

k_{v-s} ratios for many hydrocarbon and non-hydrocarbon gases were obtained experimentally from the study of ternary systems by earlier workers (1, 12, 26).

The pressure composition diagrams obtained by the statistical mechanical treatment of the solid-solution theory to the gas hydrates also give the values of equilibrium constants at 32°F for N₂, CH₄, C₂H₆, and C₂H₄. Figure 19 represents the values of equilibrium constants for CH₄ obtained from the theoretically predicted pressure-composition diagrams for the three ternary systems. Experimental values of the equilibrium constants for methane are also shown in Figure 19 for comparison. The values of the equilibrium pressures plotted in this figure are the corrected values of the pressures theoretically obtained. The values of the equilibrium constant for CH₄ at pressures of 100 to 300 psia were obtained from the data of Carson and Katz⁽¹⁾.

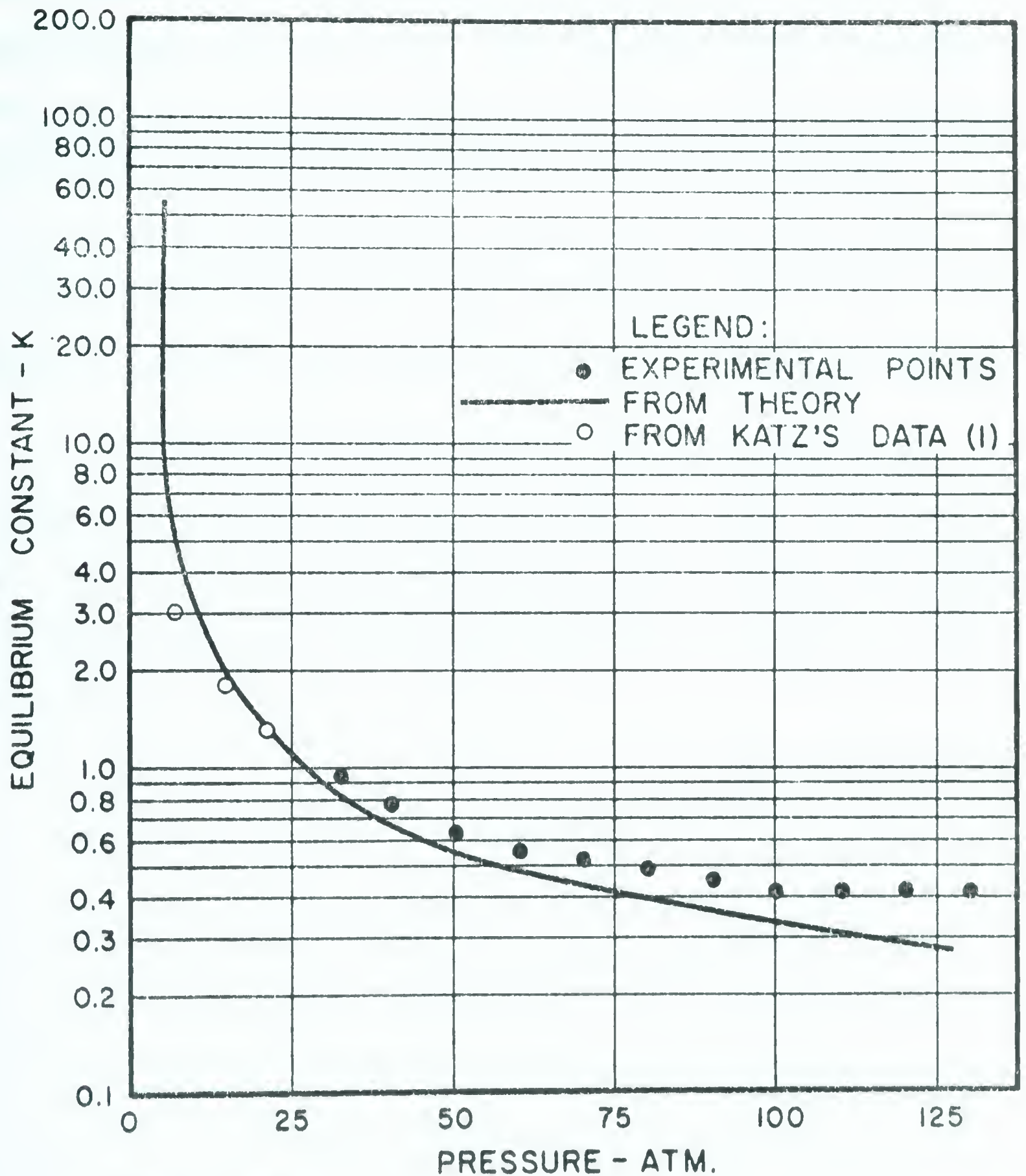


FIG. 19
EQUILIBRIUM CONSTANTS FOR METHANE
AT 32 °F

These values of equilibrium constants were slightly lower than those obtained from the theory. The agreement existing between the experimental and theoretical values of equilibrium constants, proves the ability of the statistical mechanical treatment of the solid-solution theory to predict the distribution of a component among two phases, gas and hydrate, with a fair degree of accuracy. The maximum deviation is less than 25%.

The values of equilibrium constants obtained from the experimental pressure composition data at 32°F , 39.7°F and 44°F were used in extending the equilibrium constant curves for methane in a region where the value of the equilibrium constant is less than unity.

DISCUSSION OF RESULTS

Initial Hydrate-Forming Conditions

Results on initial hydrate-forming conditions for pure nitrogen, pure methane, and mixtures of nitrogen and methane are depicted in Figure 9. It becomes apparent that the behavior of the ternary system under investigation, $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$, is very similar to that of $\text{CH}_4\text{-C}_2\text{H}_6\text{-H}_2\text{O}$ or $\text{CH}_4\text{-C}_3\text{H}_8\text{-H}_2\text{O}$ as far as initial hydrate-forming conditions are concerned. The same general trend is exhibited by $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ as regards the effect brought about by the small concentrations of the heavier component on the values of equilibrium pressures. Small amounts of methane bring about a large drop in the equilibrium pressures at the same temperatures. Equilibrium pressure responds to temperature in a manner which is similar to that exhibited by other ternary systems. It is, however, interesting to note that the slope of the $P\text{-}T$ plot shows a systematic variation as the methane content of the gas increases from zero to one hundred percent. The slope of the pressure-temperature curve for pure nitrogen is constant throughout the range of temperature studied. For a particular mixture of nitrogen and methane the slope of the pressure-temperature curve is low at lower

temperatures, but rises considerably with the rise in temperatures. Pressure-temperature curve for methane clearly exhibits this fact. It is interesting to note that the equilibrium pressures for the mixture with 87.1% CH₄ are lower than those for pure methane above 67°.

The Clapeyron equation defines the slope of a pressure temperature curve of a univariant phase-equilibrium by the following equation.

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad (27)$$

The physical process may be represented by the following equation



ΔV can be approximately equated to $\frac{ZRT}{P}$ where Z is the compressibility factor of the gas. Equation 1, after substituting for ΔV , takes the following form.

$$\frac{1}{P} \frac{dP}{dT} = \frac{\Delta H}{ZRT^2}$$

$$\therefore \frac{d \ln P}{dT} = \frac{\Delta H}{ZRT^2} \quad (29)$$

The slope of a pressure temperature curve on a semi-logarithmic plot is given by the right hand side of Equation 3. For a small temperature difference a change in the quantity '1/T²'

may be assumed to be very small (T being the absolute temperature). Consequently the slope will change according to the variation in the quantity $\frac{\Delta H}{Z}$.

ΔH at temperatures T and $T + \Delta T$ may be correlated according to the following relation assuming the applicability of Kirchhoff's law:

$$H(T + \Delta T) = \Delta H(T) + (\Delta C_p) \Delta T$$

ΔC_p is the difference in specific heats of the products and reactants. According to Equation 2, ΔC_p may be represented by the following relation.

$$\Delta C_p = n \cdot C_p(H_2O) + C_p(G) - C_p(\text{Hydrate})$$

As Gas-Hydrate is a solid phase, it can be intuitively assumed that ΔC_p is a positive quantity. Hence it can be safely assumed that ΔH rises with the rise in temperature. The variation of compressibility factors for nitrogen and methane along the pressure-temperature curves is shown in Figure 20. The compressibility factor for nitrogen rises with the rise in temperature and that for methane drops with the rise in temperature. Consequently it may be expected that the overall variation of the quantity $\Delta H/Z$ for nitrogen is insignificant, and as a result the slope of the equilibrium curve is constant. On the other hand,

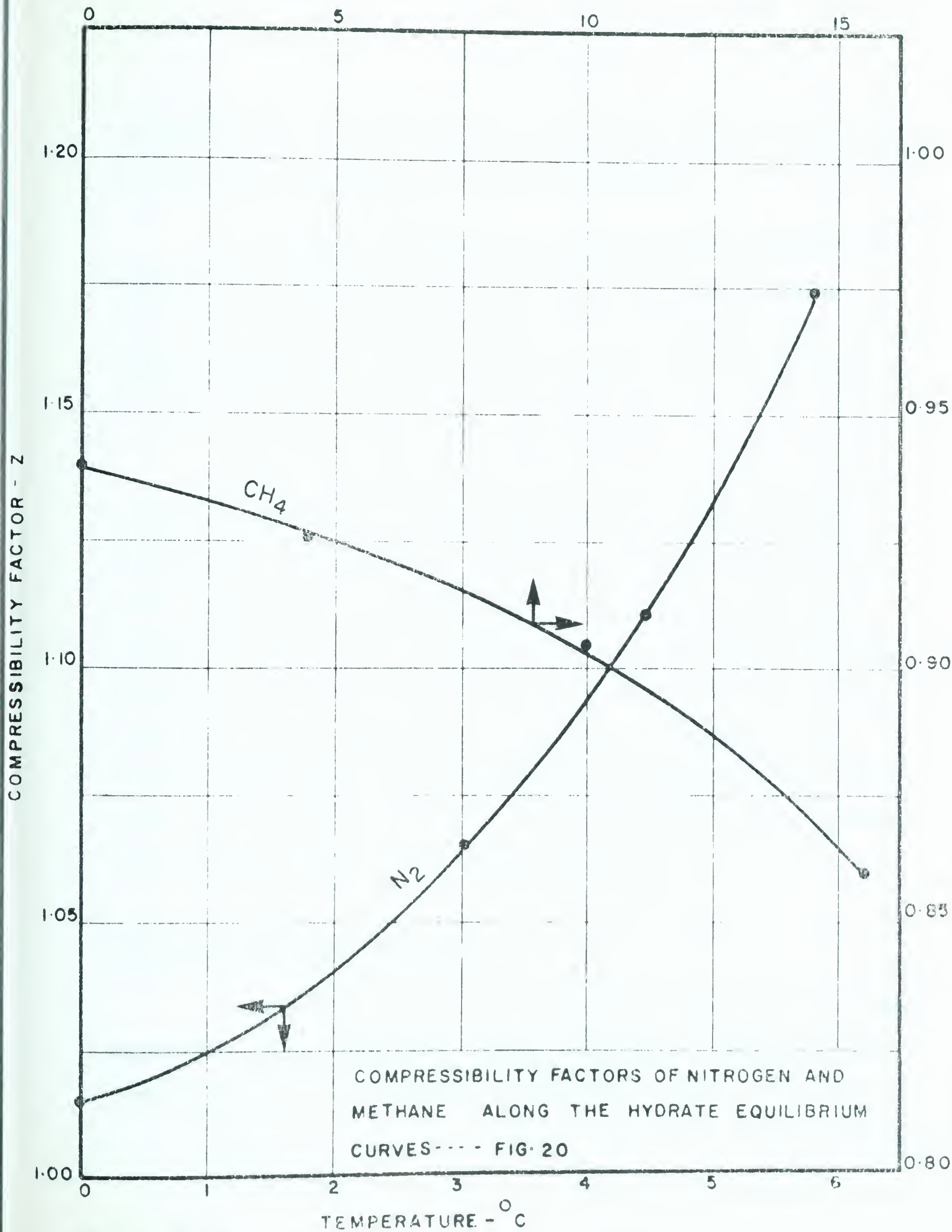


FIG. 20

variations in H and Z tend to increase the value of the slope of the pressure-temperature curve for methane.

The above discussion can be successfully applied to explain the overlapping of the pressure-temperature curves for 87.1% CH_4 gas and pure methane. It is possible that at higher temperatures the variation in $\Delta H/Z$ for 87.1% CH_4 gas is less than that for the pure gas.

This also explains the paradoxical behaviour of the variable R in Figure 22, which represents the ratio of the equilibrium pressures for a mixture and pure methane, at the same temperature. It was previously expected that R would increase with the rise in temperature for a mixture containing certain amounts of nitrogen. As a matter of fact R decreases with the rise in temperature. The smaller values of R for higher temperatures can be explained on the basis of the variations of the slope of pressure temperature curves with temperature for pure methane and a gaseous mixture.

Pressure-Composition Diagrams

Statistical mechanical treatment of the solid-solution theory of the gas-hydrates, though inadequate, describes the actual behaviour in a fairly satisfactory manner. Figure 12

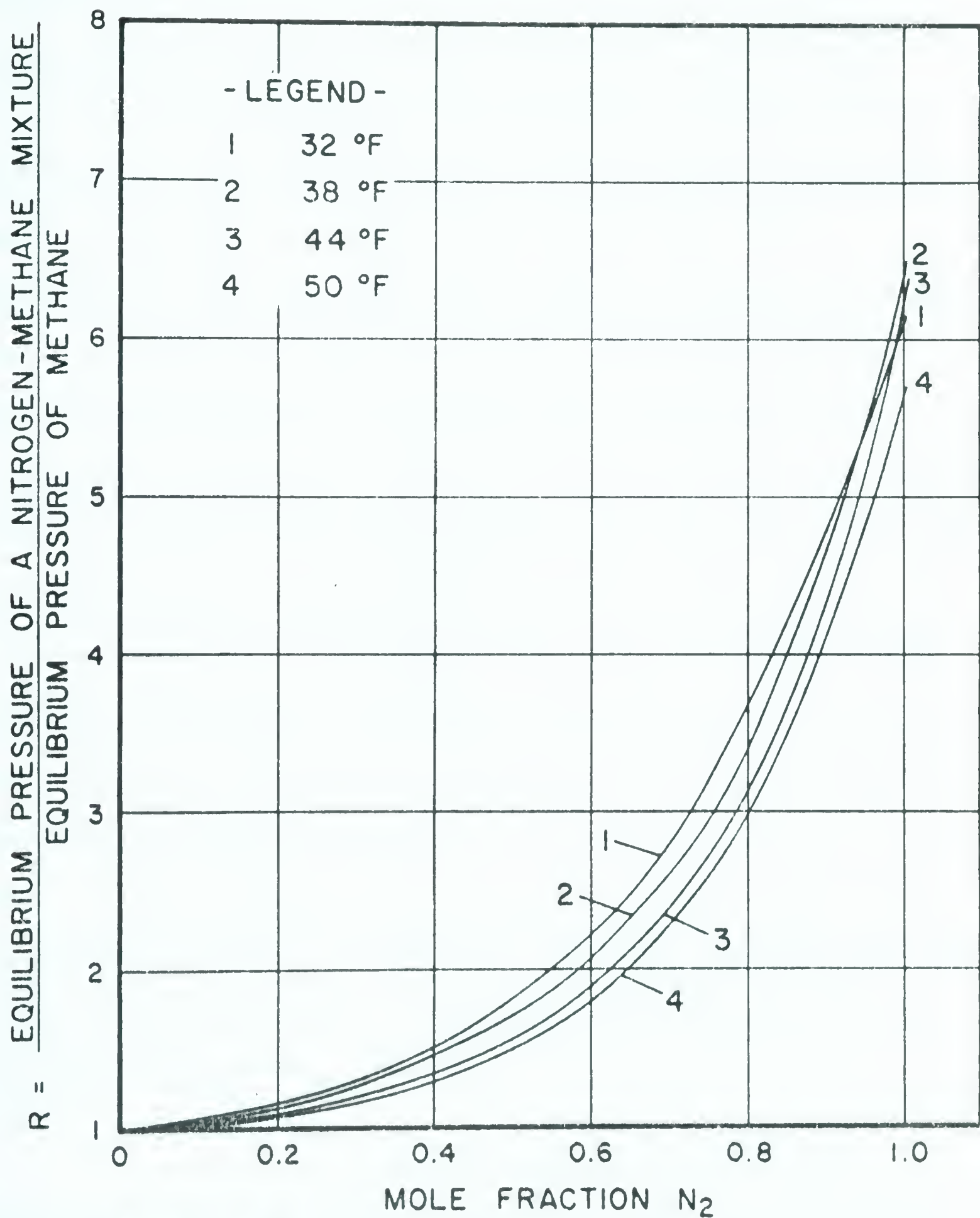


FIG. 22

EFFECT OF NITROGEN ON THE EQUILIBRIUM PRESSURE

compares the experimental pressure-composition data with those obtained from the theory at 32°F. The actual values of the equilibrium pressure predicted from the theory were corrected for the inherent defect of the potential model by an empirical formula. Considering the limitations of the experimental technique, the theory appears to handle the actual situation very well. The deficiency of the theory in predicting the pressures accurately may be attributed to the assumption of spherical shape of the molecules and central force-field. Large non-spherical molecules of nitrogen and ethane can not rotate freely in the cavities and it is thought that this hindered rotation is the cause of the large deviations in the equilibrium pressures. The general formulas for obtaining the distribution of a particular component in the gas and hydrate phases still remain applicable. The correction applied to the theoretically predicted values of equilibrium pressures using an empirical formula is essentially the same as determining the Langmuir Constants for the gases from experimental values of equilibrium pressures.

To extend the applicability of the statistical mechanical theory to large non-spherical molecules, it is necessary to obtain the Langmuir constants for the gases from the experimental values of the equilibrium pressures. Large

deviations may be anticipated if theoretically obtained values of Langmuir constants are employed in the calculations of equilibrium pressures. At this stage, the procedure employed by Van der Waals and Platteeuw⁽²⁶⁾ to obtain the modified values of Langmuir constants for propane and methane in the ternary system $\text{CH}_4\text{-C}_3\text{H}_8\text{-H}_2\text{O}$ may be worthy of a critical review. The mixed hydrates of propane and methane grow in Structure II due to the large size of the propane molecule. The fractional occupation of the cavities (larger cavities of Structure II) by SF_6 and C_3H_8 was assumed to be the same. The fractional occupation of the cavities for SF_6 was calculated from the knowledge of the equilibrium pressure of SF_6 hydrate at -3°C , and theoretical value of the Langmuir constant which is found to be 570 atm^{-1} . From this information it was possible to obtain the value of $\Delta\mu$ for Structure II.

The assumption of equal fractional occupation of the cavities by C_3H_8 and SF_6 , along with the knowledge of $\Delta\mu$ for Structure II made it possible to obtain the value of Langmuir constant for propane.

Evaluation of Langmuir constants for CH_4 entailed the adjustment of the molecular parameter ϵ/k , in order to match the experimental value of the equilibrium pressure at -3°C

with that obtained from the theory using the new value of the molecular parameter. Langmuir constants for methane in Structure II were obtained using the new value of the parameter along with other constants reported in the literature.

As Lennard-Jones potential can handle only spherical molecules satisfactorily, it is necessary to search for a potential model capable of handling non-spherical molecules, by taking into account the forces of attraction correctly without the restrictive assumption of the central force-field. Corner's potential model⁽³⁾ and Kihara's core models⁽¹⁰⁾ appear quite promising. Once the mathematical technique is established to handle these potential models, statistical mechanical treatment of non-spherical molecules can satisfactorily account for the phase behaviour of hydrates.

Equilibrium Constants

As stated earlier, statistical mechanical treatment of gas-hydrates using the Lennard-Jones potential satisfactorily predicts the distribution of a component in the gas and hydrate phases. Equilibrium constants therefore can be predicted fairly accurately from the theory. Theoretically predicted

values of equilibrium constants for methane at 32°F are compared with those obtained from the experimental results in Figure 19. Agreement among the two sets of values confirms the ability of the theory to predict equilibrium constants with a fair degree of accuracy.

OUTLINE FOR FUTURE WORK

The application of the solid solution theory to the phase behaviour of gas hydrates might include the following.

- (1) A further test of the Lennard-Jones-Devonshire theory in predicting the equilibrium constants in a ternary system consisting of gases of relatively small molecules is suggested. It might be necessary to apply an empirical correction to the predicted values of equilibrium pressures.
- (2) As the mixed hydrates of the ternary system N_2 - CH_4 - H_2O grow in Structure I, it was not necessary to adjust the molecular parameters of nitrogen. It is suggested that a ternary system consisting of nitrogen and a hydrocarbon which forms hydrates in Structure II may be studied. The theoretical investigation of such a system will necessitate the determination of the Langmuir constants for nitrogen in Structure II. It is suggested that the same technique may be used to obtain the Langmuir constants for relatively small molecules in Structure II. The prediction of the behaviour of a multicomponent system is feasible, once the Langmuir constants are available.

- (3) The evaluation of the constant ' g_k ' for various gases may be undertaken with a view to compile a list of the Langmuir constants which can be used to predict equilibrium constants.
- (4) For a satisfactory explanation of the behavior of non-spherical molecules in cavities it is necessary to apply potential models which correctly account for the forces of attraction without the assumption of the central force-field. Kihara's core models and Corner's potential model may be successfully applied for the prediction of phase-behavior of hydrates.

NOMENCLATURE

a	Cell radius
C	Number of components
C_p	Heat Capacity
C_{ki}	Langmuir constant of a k molecule in a type i cavity
F	Number of degree of freedom
F	Free energy/mole
g	A measure of the free volume of the solute molecule wandering in the cavity
g_s	Degeneracy of the energy state i
G.P.F.	Grand partition function
h_{Ji}, h_{Ki}	Partition function of a J (or K) molecule in a type i cavity
H	Hydrate phase
H	Enthalpy/mole
I	Ice phase
k	Boltzmann's constant
k_{v-s}	Equilibrium constant
L_1	Liquid phase rich in water
L_2	Liquid phase rich in hydrate former
P	Number of phases
P_J, P_K	Partial pressure of J or K component gas
Q	Partition function

R	A gas capable of hydrate formation
T	Absolute temperature
V	Volume
x	Mole fraction of a gas
y	Mole fraction of a gas in the gas phase
Y_{ki}	Probability of finding a K molecule in a cavity of type i.
Z	Number of oxygen atoms surrounding the two types of cavities
Z	Compressibility factor
α	Stable modification of water (ice or liquid water)
α	A dimensionless parameter of the cell geometry
β	Metastable modification of water
γ_i	Number of cavities of the ith type per water molecule
ϵ_i	Energy of the state i
Φ_K	Partition function of a K molecule with the volume factor removed
λ	Absolute activity
μ	Chemical potential
σ	A molecular parameter

BIBLIOGRAPHY

1. Carson, D.B., D.L. Katz: Trans. AIME, 146, 150 (1942).
2. Claussen, W.F.: J. Chem. Phys. 19, 1425 (1951).
3. Curtiss, C.F., J.O. Hirschfelder, R.B. Bird: "Molecular Theory of Gases and Liquids", John Wiley, (1955).
4. Deaton, W.M., E.M. Frost: Oil and Gas Journal, 45 (12), 170-178, (1948).
5. Deaton, W.M., E.M. Frost: U.S. Bureau Mines Monograph, 8, (1946).
6. Forcrand, R. de, Compt. Rend., 106, 849, (1939).
7. Hammerschmidt, E.G.: Ind. Eng. Chem., 26, 857 (1934).
8. Katz, D.L., et al: Natural Gas Engineering Handbook, McGraw-Hill, pp. 211 (1959).
9. Keys, F.G., H.G. Burks: Journal of American Chemical Society, 50, 1100 (1928).
10. Kihara, T.: Reviews of Modern Physics, 25, (4), 831 (1953).
11. Lennard, Jones J.E., A.F. Devonshire: Proc. Roy. Soc. (London) A 163, 53 (1937): A 165 (1938).
12. Noaker, L.J., D.L. Katz: Trans. AIME, 201, 237 (1954).
13. Otto, F.D.: M.Sc. Thesis, University of Alberta (1959).
14. Palin, D.E., H.M. Powell: Nature 156, 334 (1945).
15. Powell, H.M.: Rec. trav. chim. 75, 855 (1956).
16. Perry, J.H.: Chemical Engineers' Handbook, McGraw-Hill, pp. 68, (1949).
17. Roberts, Brownscome, Howe: Oil and Gas Journal, 39 (30), 37 (1940).

18. Robinson, D.B.: Application of the Phase Rule to Study of Natural Gas-Hydrates, Unpublished report, (1947).
19. Scheffer, F.E.C., G. Meyer: Proc. Acad. Sci. Amsterdam 21, 1204, 1338 (1919).
20. Schroder, W.: Die Geschichte der Gashydrate, F. Enke, Stuttgart, 1920.
21. Snell, E.: M.Sc. Thesis, University of Alberta (1961).
22. Sortland, L.D.: M.Sc. Thesis, University of Alberta (1962).
23. Stackelberg, M. Von, H.R. Mueller, Z. Electrochem., 58, 25 (1954).
24. Stackelberg, M. Von, W. Meinhold, Z. Electrochem., 58, 40 (1954).
25. Stackelberg, M. Von, H. Fruhbuss, Z. Electrochem., 58, 99 (1954).
26. Unruh, C.H., D.L. Katz: Trans. AIME 186, 83 (1949).
27. Van Cleeff, A., G.A.M. Diepen, Rec. trav. Chim. 79, 58, (1960).
28. Waals, J.H. Van der, J.C. Platteeuw: "Clathrate Solutions", Advances in Chemical Physics, Vol. II, p. 2 (1960).
29. Ibid, Vol. II, p. 9, (1960).
30. Ibid, Vol. II, p. 32 (1960).
31. Ibid, Vol. II, p. 47 (1960).
32. Villard, P., Compt. rend., 106, 1602 (1888).
33. Wilcox, W.I., D.B. Carson, D.L. Katz: Ind. Eng. Chem., 33, 662 (1941).

APPENDIX

APPENDIX A

Calculation of Compressibility Factors for Nitrogen-Methane Mixtures

As no adequate data on the compressibility factors of N_2-CH_4 mixtures were found in literature, it was decided to use an equation of state proposed by Keys and Burks⁽⁹⁾ to obtain the compressibility factors for mixtures. The constants for the mixtures were obtained by a linear combination of the constants of pure components.

The equation of state, when applied to mixtures has the following form,

$$P = \frac{\sum R_i w_i T}{V - \sum B_i - \frac{\sum \alpha_i w_i}{V}} - \frac{(\sum A_i w_i)^2}{(V + \sum l_i w_i)^2} \quad (1)$$

where,

P = Pressure in atmosphere

R_i = Universal gas constant of the
ith component in the ($\frac{\text{atm. cc.}}{\text{gm. OK}}$)
mixture

w_i = weight fraction of the ith component in
the mixture

T = Temperature $^{\circ}K$

V = Volume, cc/gm.

$A_i, B_i \propto_i, l_i$ = constants of the ith component in an equation
of state.

The constants for nitrogen and methane are as follows:

	<u>Methane</u>	<u>Nitrogen</u>
A	10151.40	1650.50
B	3.961	1.65
α	2.857	0.992
l	0.536	0.313
R	5.1173	2.9286

The constants for mixtures were obtained by using the following rules.

$$A_{\text{mix.}} = (A_{\text{nitrogen}} \times w_{\text{N}_2} + A_{\text{CH}_4} \times w_{\text{CH}_4})^2$$

$$B_{\text{mix.}} = B_{\text{N}_2} \times w_{\text{N}_2} + B_{\text{CH}_4} \times w_{\text{CH}_4}$$

$$\alpha = \alpha_{\text{N}_2} \times w_{\text{N}_2} + \alpha_{\text{CH}_4} \times w_{\text{CH}_4}$$

$$l = l_{\text{N}_2} \times w_{\text{N}_2} + l_{\text{CH}_4} \times w_{\text{CH}_4}$$

$$R = R_{\text{N}_2} \times w_{\text{N}_2} + R_{\text{CH}_4} \times w_{\text{CH}_4}$$

writing,

$$P_{R_1} \text{ and } P_{R_2} \text{ for } \frac{\sum R_i w_i}{V - \sum R_i e^{-\frac{\sum \alpha_i w_i}{V}}} \text{ and } \frac{(\sum \sqrt{A_i} w_i)^2}{(V + \sum l_i w_i)^2}$$

respectively, Equation I takes the following form:

$$P = P_{R_1} T - P_{R_2} \quad (\text{II})$$

$$\text{or } Z = \frac{PV}{RT} = \frac{P_{R1} \cdot V}{R} - \frac{P_{R2} \cdot V}{RT} \quad (\text{III})$$

The values of P_{R1} and P_{R2} were computed on the Computer IBM 1620, covering a range of volume for 5 to 60 cc/gm. Using these values of P_{R1} and P_{R2} , compressibility factors at any temperature can be obtained.

Vol.	8% N ₂		20% N ₂		32% N ₂	
	P _{R1}	P _{R2}	P _{R1}	P _{R2}	P _{R1}	P _{R2}
5	1.763	302.310	1.629	261.072	1.497	222.501
15	0.417	38.225	0.388	32.805	0.361	27.783
25	0.229	14.136	0.214	12.115	0.200	10.246
35	0.157	7.296	0.1474	6.250	0.138	5.283
45	0.119	4.443	0.112	3.804	0.105	3.214
55	0.0961	2.986	9.059	2.556	0.085	2.159

44% N ₂		56% N ₂		68% N ₂		
5	1.366	186.678	1.2377	153.689	1.1128	123.63
15	0.334	23.162	0.3079	18.947	0.2824	15.143
25	0.1864	8.530	0.1728	6.969	0.1594	5.562
35	0.1289	4.395	0.1198	3.588	0.1109	2.862
45	0.0984	2.673	0.0917	2.1822	0.0850	1.740
55	0.0796	1.796	0.0742	1.465	0.0688	1.168

80% N ₂		
5	0.9923	96.580
15	0.2575	11.754
25	0.1464	4.3113
35	0.1021	2.2175
45	0.0783	1.3475
55	0.0636	0.9046

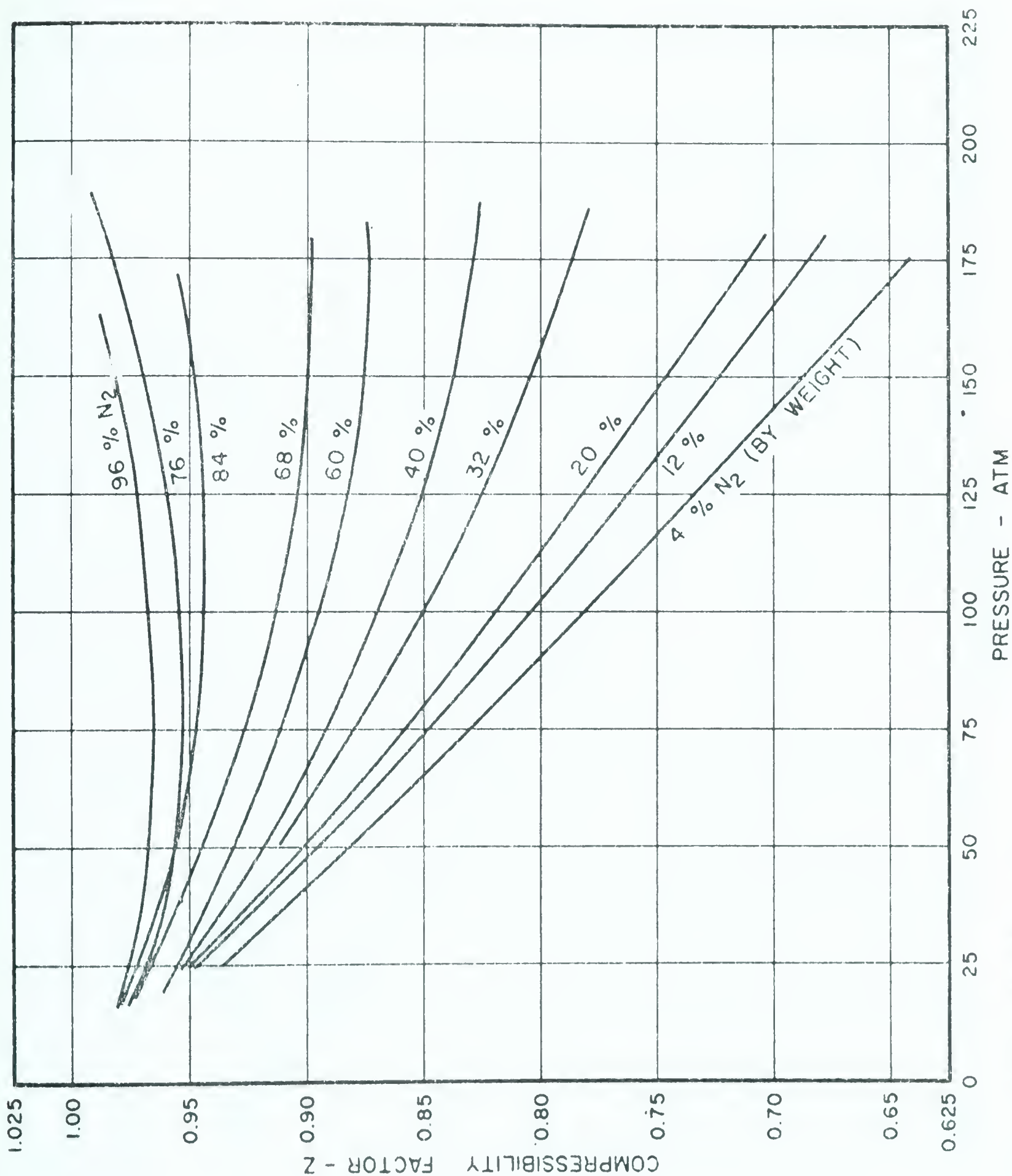


FIG. 21 A
COMPRESSIBILITY FACTORS OF N_2-CH_4 SYSTEM AT 32 °F

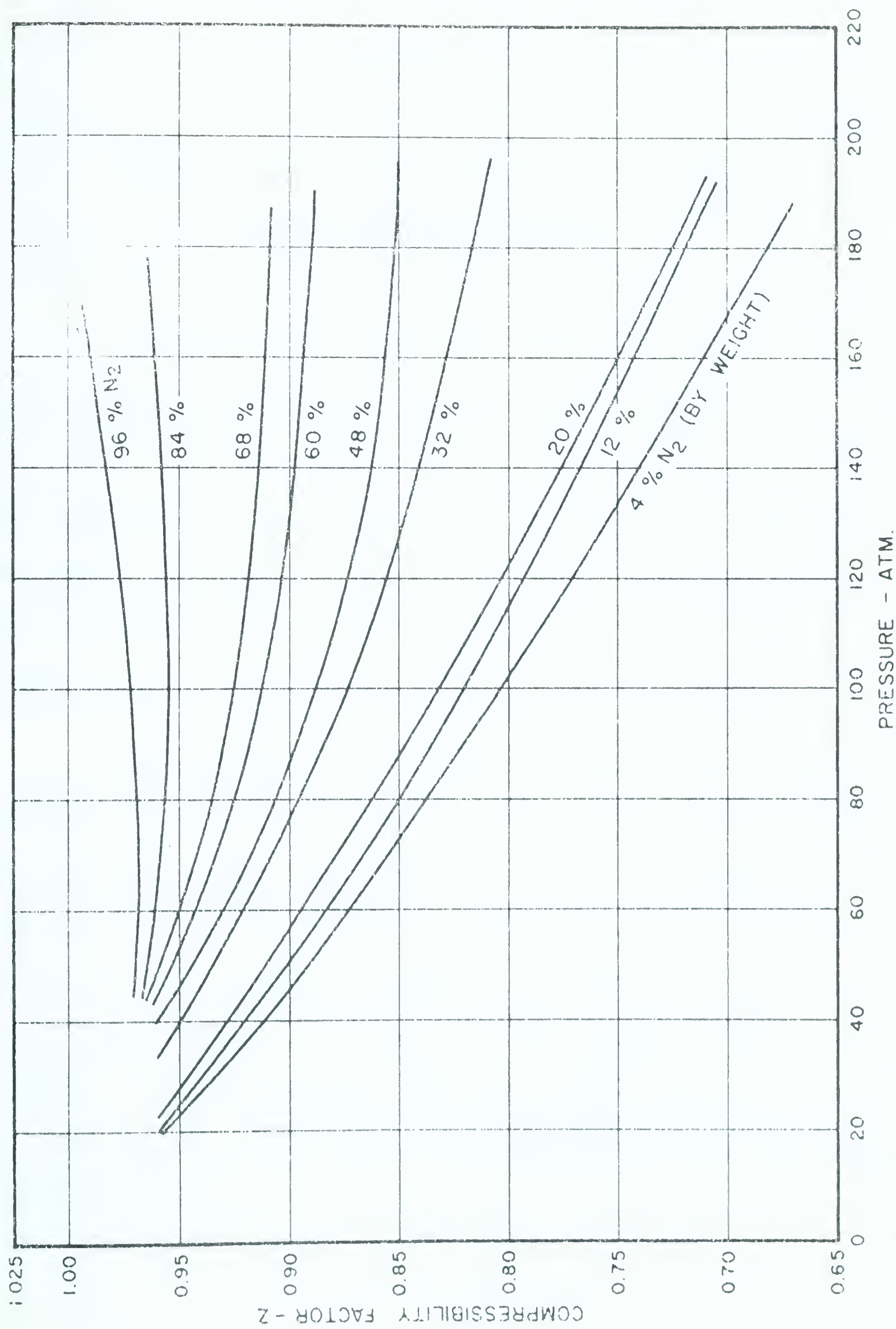


FIG. 21
COMPRESSIBILITY FACTORS OF N_2-CH_4 SYSTEM AT $44^\circ F$

APPENDIX B

Determination of the Composition of the Hydrate

Phase by Material Balance

As the technique employed for the analysis of the hydrate phase was likely to give inaccurate results due to the difficulties in maintaining truly isobaric conditions and the possibility of the gas occlusion in the hydrate phase, it was decided to develop a formula based on the material balance of the system, for the determination of the hydrate phase composition.

As stated earlier, a certain charge consisting of nitrogen and methane was compressed to a predetermined pressure by injecting mercury into the cell. During the process of hydrate formation the level of mercury in the cell was maintained, so as to keep the volume of the cell above the level at a constant value. As a result of the hydrate formation the pressure of the gas dropped from the initial value of P_1 to P_2 . The samples of the gas at the beginning and end were analysed chromatographically.

If Y_1 and Y_2 are the mole fractions of nitrogen at the initial and final conditions; and Z_1 , Z_2 are the compressibility factors at the initial and final conditions, the number of moles of nitrogen transferred from the gas phase to the hydrate phase is,

$$M_1 = \frac{P_1 V_0}{Z_1 R T_0} \cdot Y_1 - \frac{P_2 V_0}{Z_2 R T_0} \cdot Y_2 \quad (I)$$

where V_0 and T_0 are the constant volume and temperature of the system.

The total number of moles of gas transferred to the hydrate phase is,

$$M_2 = \frac{P_1 V_0}{Z_1 R T_0} - \frac{P_2 V_0}{R Z_2 T_0} \quad (II)$$

Therefore, the mole fraction of nitrogen in the hydrate phase is given by,

$$x = \frac{M_1}{M_2} \cdot \frac{\frac{P_1}{Z_1} Y_1 - \frac{P_2}{Z_2} \cdot Y_2}{\frac{P_1}{Z_1} - \frac{P_2}{Z_2}} \quad (III)$$

It is assumed that the change in volume of the system due to the formation of hydrate is negligibly small, and as a result, the volume of the system remains constant. As the solubility of the gas in the water phase is small, no correction was made in the derivation of the relation (III).

The accurate estimation of 'x' requires the compressibility factor data with a high degree of reliability. As no adequate experimental data on the compressibility factor of nitrogen-methane mixtures were available, an equation of state (9) was employed to evaluate them. Consequently, the reliability of the calculated values of 'x' using those values of compressibility factors is reduced. The relation (III) was therefore used with caution in this investigation.

SAMPLE CALCULATION

The application of the Equation III is illustrated below for the evaluation of the hydrate phase composition. The following set of data were obtained from a run made at 32°F.

Initial pressure = p_1 = 1223 psia

Final pressure = p_2 = 948 psia

Mole percent N_2 in the initial charge = Y_1 = 56.0

Mole percent N_2 in the gas phase = Y_2 = 64.3

at equilibrium

Mole percent N_2 in hydrate phase = x_{act} = 35.3

Compressibility factor of the initial charge (Fig. 21)
= Z_1 = 0.925

Compressibility factor of the gas at equilibrium = Z_2 = 0.955

$$x_{cal.} = \frac{\frac{1030}{0.914} \times 0.439 - \frac{780}{0.938} \times 0.526}{\frac{1030}{0.914} - \frac{780}{0.938}} = 0.298$$

Mole percent N_2 in the hydrate phase by calculation
is 29.8

The further application of the Equation III is illustrated through the following table where the calculated values of the

hydrate composition are compared with the actual values of the hydrate phase compositions from the experimental data at 32°F.

<u>P₁</u> <u>psia</u>	<u>P₂</u> <u>psia</u>	<u>Y₁</u> <u>Mole % N₂</u>	<u>Y₂</u> <u>Mole % N₂</u>	<u>x_{cal.}</u> <u>Mole % N₂</u>	<u>x_{act.}</u> <u>Mole % N₂</u>
1030.0	780.0	49.9	53.0	19.0	20.0
2240.0	1860.0	85.3	90.0	62.2	76.5
930.0	524.0	9.6	16.0	2.5	6.5
2421.0	1930.0	90.6	92.5	83.5	81.0
1224.0	948.0	56.0	64.5	29.8	35.0
1796.0	1540.0	75.9	81.5	59.5	62.0
2638.0	2128.0	91.5	94.0	81.8	86.0

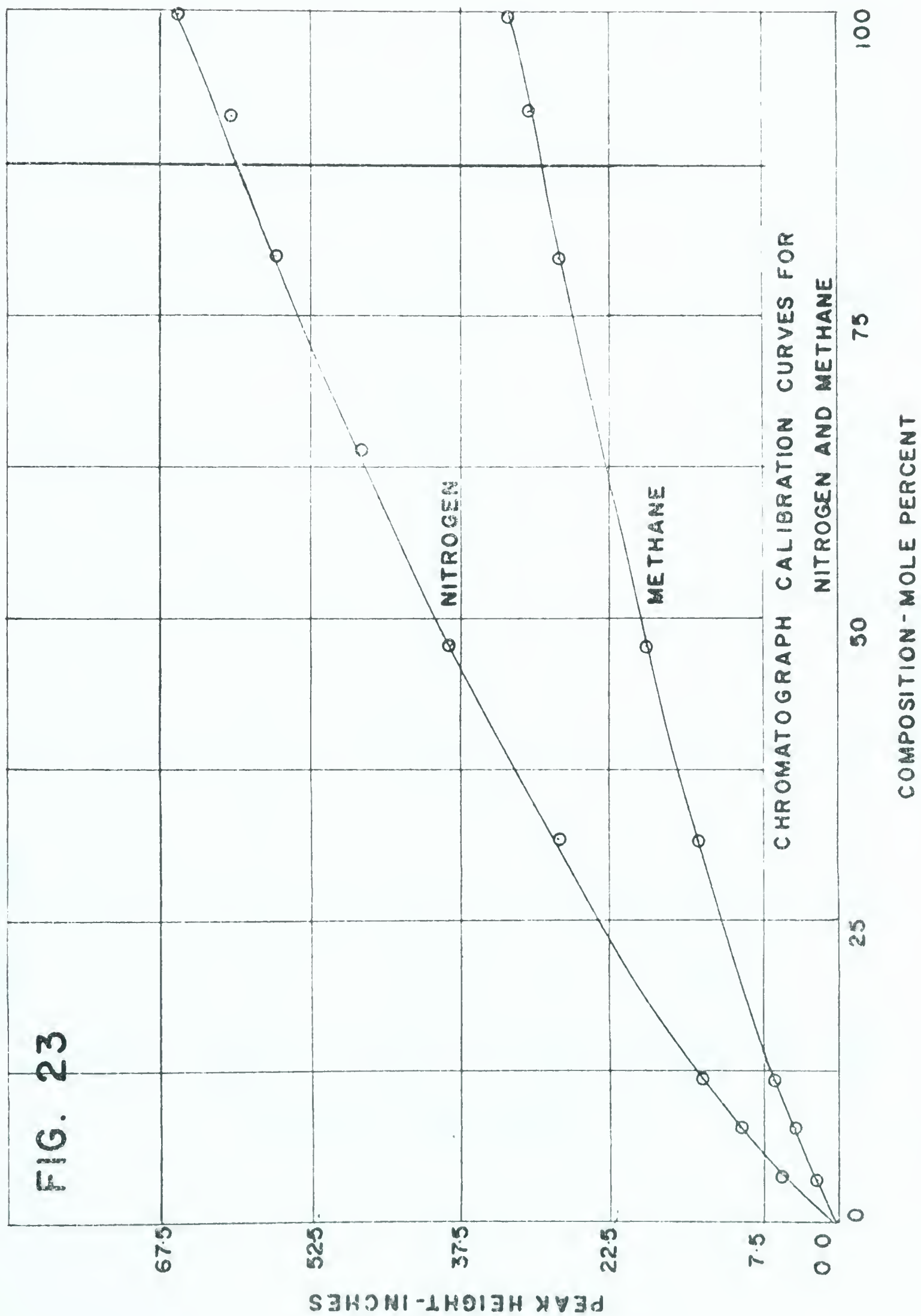
APPENDIX C

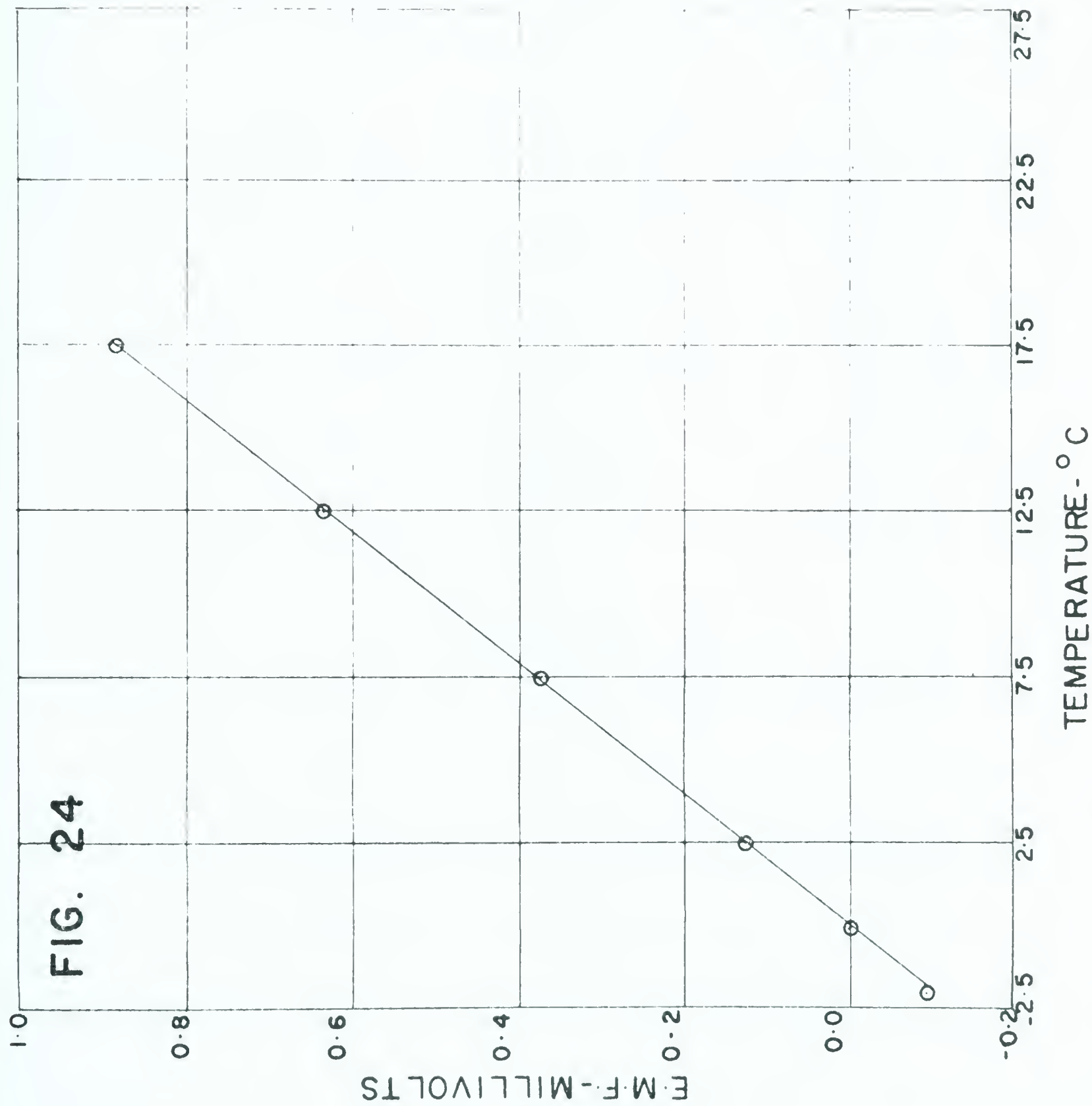
Chromatographic Analysis

The technique of gas-liquid partition chromatography was employed for the analysis of the gas samples consisting of nitrogen and methane. The Kromo-tog model K-2 manufactured by the Burrell Corporation was used with a 2½ meter Linde Molecular Sieve (13-x) Column. One meter long column could not separate the oxygen peak from the nitrogen peak. It was necessary to have both the peaks distinctly separate so as to know if there is any impurity in the gas sample. Helium gas with a flow rate of 45 ml/min was employed as a carrier gas. A cell current of 160 mA was used. Peak heights were used for calibration.

Fluctuations in the room temperature had a marked influence on the peak heights. At times the analysis showed a total percent of more than one hundred. The values of the mole percents of each of the components were corrected to obtain a total value of one hundred. A similar correction was applied by earlier workers^(19,20).

FIG. 23





IRON-CONSTANTAN THERMOCOUPLE CALIBRATION

APPENDIX D

TABULATIONS

TABLE I

EXPERIMENTAL DATA ON INITIAL HYDRATE-FORMING
CONDITIONS FOR THE N_2 - CH_4 - H_2O SYSTEM

<u>Composition - Mole % Methane</u>	<u>Pressure psia</u>	<u>Temperature °F</u>
100	385.0	32.0
	605.0	40.0
	810.0	45.0
	1257.0	52.7
	1690.0	57.4
	2039.0	60.4
	2916.0	65.4
	4143.0	70.1
87.2	1073.0	49.3
	1350.0	52.5
	2106.0	58.2
	2481.0	61.4
	2537.0	63.0
	2831.8	64.1
	2900.0	65.0
	3326.8	67.5
	3576.5	68.5
73.1	565.0	32.0
	1298.0	50.3
	1918.0	56.6
	2835.0	62.2
	3769.0	66.5
	4980.0	70.3
50.25	720.0	32.0
	890.0	39.3
	1127.0	43.7
	1521.0	48.5
	2596.0	57.5
	3625.0	62.0
	4814.0	65.6

TABLE I (Con't.)

<u>Composition - Mole % Methane</u>	<u>Pressure psia</u>	<u>Temperature °F</u>
27.2	1155.0	32.0
	1474.0	39.0
	1833.0	44.3
	2472.0	49.5
	2538.0	50.0
	3005.0	53.5
	3647.0	56.5
	4132.0	58.7
24.0	1250.0	32.0
	1327.0	34.5
	1880.0	41.2
	2530.0	48.0
	3530.0	53.5
	4640.0	58.0
	5215.0	60.7
10.8	1820.0	32.0
	2300.0	39.2
	2812.0	42.7
	3266.0	46.0
	3745.0	48.0
	4175.0	50.0
100% N ₂	2360.0	32.0
	2485.0	33.0
	2775.0	35.2
	3436.0	38.0
	3655.0	39.7
	4150.0	41.7
	4390.0	43.0
	5100.0	46.3

TABLE IA

ISOTHERMAL DATA ON INITIAL HYDRATE FORMING CONDITIONS

T = 32°F		T = 38°F		T = 44°F	
<u>Pressure</u> <u>psia</u>	<u>y % N₂</u>	<u>Pressure</u> <u>psia</u>	<u>y % N₂</u>	<u>Pressure</u> <u>psia</u>	<u>y % N₂</u>
2360.0	100.0%	3320.0	100.0%	5350.0	100.0%
1820.0	89.2%	2210.0	89.2%	3000.0	89.2%
1250.0	76.0%	1580.0	76.0%	2850.0	76.0%
1155.0	72.8%	1400.0	72.8%	1830.0	72.8%
720.0	49.8%	870.0	49.8%	1150.0	49.8%
565.0	26.9%	680.0	26.9%	880.0	26.9%
382.0	0.0%	520.0	0.0%	740.0	0.0%

T = 50°F		T = 56.0°F	
<u>Pressure</u> <u>psia</u>	<u>y % N₂</u>	<u>Pressure</u> <u>psia</u>	<u>y % N₂</u>
4200.0	89.2%	4100.0	76.0%
2850.0	76.0%	3530.0	72.8%
2500.0	72.8%	2330.0	49.8%
1600.0	49.8%	1820.0	26.9%
1225.0	26.9%	1520.0	0.0%
1060.0	0.0%		

TABLE IB

ISOBARIC DATA ON INITIAL HYDRATE FORMING
CONDITIONS FOR THE $N_2-CH_4-H_2O$ SYSTEM

<u>Pressure</u> <u>psia</u>	<u>Temperature</u> <u>°F</u>	<u>Mole % CH₄</u>
1000	40.5	50.3
	45.0	73.1
	47.5	87.2
	49.0	100.0
1500	36.5	24.0
	39.5	27.2
	48.5	50.3
	52.5	73.1
	54.0	87.2
2000	35.0	10.8
	43.0	24.0
	46.0	27.2
	53.5	50.3
	57.0	87.2
	59.0	100.0
2500	33.0	0.0
	40.5	10.8
	47.5	24.0
	50.0	27.2
	57.0	50.3
	60.5	87.3
	63.3	100.0

TABLE II

EXPERIMENTAL PRESSURE COMPOSITION DATA
FOR THE $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ SYSTEM AT 32°F

<u>Pressure atm.</u>	<u>Mole % N_2 in the gas phase</u>	<u>Mole % N_2 in the hydrate phase</u>
26.1	0.0	0.0
35.7	16.0	6.5
42.5	31.0	9.8
52.8	53.0	20.0
64.6	64.5	35.0
76.5	72.5	42.5
105.0	81.5	62.0
115.0	88.0	71.0
126.0	90.0	76.5
131.5	92.5	81.0
144.0	94.0	86.0
160.0	100.0	100.0

TABLE III

EXPERIMENTAL PRESSURE COMPOSITION DATA
OF THE $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ SYSTEM AT 44°F

<u>Pressure</u> <u>atm.</u>	<u>Mole % N_2 in the</u> <u>gas phase</u>	<u>Mole % N_2 in the</u> <u>hydrate phase</u>
50.7	0.0	0.0
70.5	35.0	9.1
82.6	46.0	22.4
153.5	75.0	55.0
204.0	84.0	68.0
249.0	91.4	80.2
320.0	100.0	100.0

TABLE IV

EXPERIMENTAL PRESSURE COMPOSITION DATA FOR THE
 $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ SYSTEM AT 39.7°F

<u>Pressure atm.</u>	<u>Mole % N_2 in the gas phase</u>	<u>Mole % N_2 in the hydrate phase</u>
38.1	0.0	0.0
51.3	44.0	18.0
80.0	63.0	31.0
102.0	74.0	47.0
119.0	78.0	56.0
248.5	100.0	100.0

TABLE V

PRESSURE COMPOSITION DATA FOR THE $\text{N}_2\text{-CH}_4\text{-H}_2\text{O}$ SYSTEM
AT 32°F FROM THEORY

y = mole per cent nitrogen in the gas phase

x = mole per cent nitrogen in the hydrate phase

P = theoretically predicted pressure - atm.

$$P_{\text{Corr}} = \text{corrected pressure} = p \left(y \cdot \frac{160}{90} + (1-y) \frac{26.10}{18.80} \right)$$

k = equilibrium constant = y/x

<u>y</u>	<u>P</u>	<u>P_{Corr}</u>	<u>k_{N_2}</u>	<u>k_{CH_4}</u>
0	18.8	26.1		1.000
5	19.5	27.1	4.460	0.1960
20	22.3	32.1	3.841	0.845
40	27.3	42.0	3.140	0.687
60	35.4	57.0	2.430	0.531
80	50.1	85.5	1.785	0.363
100	90.0	160.0	1.000	

TABLE VI

PRESSURE COMPOSITION DATA FOR THE $\text{CH}_4\text{-C}_2\text{H}_6\text{-H}_2\text{O}$ SYSTEM
AT 32°F FROM THEORY

y = mole per cent CH_4 in the gas phase

x = mole per cent CH_4 in the hydrate phase

P = theoretically predicted pressure - atm.

$$P_{\text{Corr}} = \text{corrected pressure} = p \left(y \cdot \frac{26.1}{18.8} + (1-y) \frac{5.20}{1.10} \right)$$

k = equilibrium constant = y/x

<u>y</u>	<u>x</u>	<u>P</u>	<u>P_{Corr}</u>	<u>k_{CH₄}</u>
0	0.000	1.10	5.20	
5	0.084	1.13	5.70	59.00
20	1.450	1.43	5.75	13.80
50	5.590	2.08	6.30	8.95
80	18.800	4.26	9.20	4.26
95	52.750	11.04	16.92	1.80
100	100.000	18.80	26.10	1.00

TABLE VII

PRESSURE COMPOSITION DATA FOR THE CH₄-C₂H₄-H₂O SYSTEM
AT 32°F FROM THEORY

y = mole per cent methane in the gas phase

x = mole per cent methane in the hydrate phase

P = theoretically predicted pressure - atm.

$$P_{\text{Corr}} = \text{corrected pressure} = p \left(y \cdot \left(\frac{26.10}{18.80} \right) + (1-y) \frac{5.44}{0.50} \right)$$

k = equilibrium constant = y/x

<u>y</u>	<u>x</u>	<u>P</u>	<u>P_{Corr}</u>	<u>k_{CH₄}</u>
0	0	0.50	5.44	
5	0.179	0.53	5.46	28.80
20	0.824	0.62	5.58	24.30
35	1.740	0.76	5.71	21.10
50	3.170	0.97	5.95	15.80
65	5.680	1.35	6.35	11.45
80	11.100	2.22	7.16	7.21
95	34.400	6.37	11.76	2.76
100	100.000	18.80	26.10	1.00

TABLE VIII

COMPRESSIBILITY FACTORS OF NITROGEN AND METHANE
ALONG THE HYDRATE-EQUILIBRIUM CURVES

NITROGEN

<u>Pressure</u> <u>atm.</u>	<u>Temperature</u> <u>°C</u>	<u>Compressibility Factor</u>
168.5	0.5	1.022
185.0	1.5	1.037
207.0	2.5	1.054
230.4	3.5	1.078
255.0	4.5	1.125
279.0	5.5	1.158

METHANE

<u>Pressure</u> <u>atm.</u>	<u>Temperature</u> <u>°C</u>	<u>Compressibility Factor</u>
29.6	1.5	0.935
36.1	3.5	0.929
44.0	5.5	0.923
61.3	8.5	0.911
74.9	10.5	0.901
93.5	12.5	0.887
134.5	15.5	0.860

APPENDIX E

The Computer Programme for the Determination of
the Pressure Composition Diagram

```
10  Read, CMA, CMB, CNA, CNB
    DELMU = EXPF (7.04)
        X = 0.05
    DELTX = 0.05

20  ALPHA = CMA * X + CNA * (1. - X)
    BETA  = CMB * X + CNB * (1. - X)
    CHI   = (3. * BETA + ALPHA)/(4. * (ALPHA * BETA ** 3.))
    GAMMA = (BETA ** 3 + 3. * ALPHA * BETA ** 2)
            (4. * (ALPHA * BETA ** 3))
    PHI   = (3. * BETA ** 2 + 3 * ALPHA * BETA)
            (6. * (ALPHA * BETA ** 3))
    ZETA  = (1. -DELMU)/(ALPHA * BETA ** 3)
    G     = GAMMA ** 2 - PHI
    H     = PHI ** 3 + CHI ** 2 - 2*PHI*GAMMA*CHI + ZETA*G
    HA    = (4.*GAMMA*CHI)/(3. - PHI**2 - ZETA/3
    C     = H + SQRTF (H**2 + HA**3)
    D     = H - SQRTF (H**2 + HA**3)

    If (C - 0.0) 23, 24, 24

23  A     = - ((-C)**0.3333/2.)
        Go to 27
```


24 A = ((C)**0.3333/2.)

27 If (D - 0.0) 25, 26, 26

25 B = - ((-D)**0.3333/2.)

Go to 28

26 B = ((D)**0.3333/2.)

28 HB = A + B

U = G + HB

V = 2.*G - HB

W = 4.*U**2 + 3.*HA - 12.*G*HB

PUNCH, U, V, W

U = SQRTF (U**2)

V = SQRTF (V**2)

W = SQRTF (W**2)

30 R₁ = - GAMMA + SQRTF (U) + SQRTF (V + SQRTF (W))

R₂ = - GAMMA + SQRTF (U) - SQRTF (V + SQRTF (W))

R₃ = - GAMMA - SQRTF (U) + SQRTF (ABSF (V - SQRTF (W)))

R₄ = - GAMMA - SQRTF (U) - SQRTF (ABSF (V - SQRTF (W)))

PUNCH, R₁, R₂, R₃, R₄

If (X - 1.) 45, 10, 10

45 X = X + DELTX

Go to 20

END

*CMA, CMB are the Langmuir Constants of gas M in Small and Large Cavity.
CNA, CNB are the Langmuir Constants of gas N in Small and Large Cavity.
DELMU = $23[\Delta H/RT]$; X = mole fraction of M in gas phase - .*

B29806